

# Structure and Relaxation of Amorphous Molecular Systems Studied by Transformation between Conformation Isomers

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1,2-dichloroethane (DCE) is a famous compound, the molecule of which takes trans and gauche conformations (Fig. 1). The former is stable in gas and crystal states, while the latter is stable in liquid state. We studied the structure of amorphous state of DCE and its relaxation process due to temperature elevation by Raman spectroscopy.

The amorphous samples were prepared by vapor deposition onto a cold metal substrate in a vacuum chamber with the base pressure below  $10^{-7}$  Pa. The thickness of the samples was made to be about 10  $\mu\text{m}$ . Raman measurements were carried out using an  $\text{Ar}^+$  ion laser at 514.5 nm with a power of 40 mW.

Figure 2 shows the C-Cl stretching-region of Raman spectra of DCE in different states. Bands marked with g and t indicate the existence of gauche and trans isomers, respectively. Spectra of gas, liquid, and crystal states have been studied well and indicate that two isomers coexist in the gas and liquid states, but only the trans isomer exists in the crystal state. We found that two isomers coexist in amorphous states. We estimated then the mole fraction of isomers from the band intensities.

Figure 3 shows the evolution of the mole fraction of gauche isomer in the amorphous samples of DCE deposited at different substrate temperatures. The temperature of each sample was elevated at a constant rate of  $0.28 \text{ K min}^{-1}$  after the deposition. Temperature dependence of corresponding mole fraction estimated for fictitious supercooled liquid is also shown by a dashed line for comparison. We found that the gauche mole fraction in the initial sample immediately after the depositions is larger as the substrate temperature is higher. The initial gauche mole fractions of the samples deposited at 30 and 43 K correspond to that of room-temperature source vapor (0.22). These results indicate that molecules are immediately frozen at deposition when the substrate temperature is sufficiently low, but can move toward the more stable conformation when the substrate temperature is relatively high. We also found that the mole fraction increased, except for the sample deposited at 82 K, toward the value estimated for supercooled liquid as the sample temperature was elevated. The abrupt decreases in gauche mole fraction around 110 K are due to the crystallization of amorphous samples. These results suggest that molecular circumstances in the amorphous samples relaxed toward that in liquid before crystallization.

The manner of the evolution of mole fraction is slightly different for samples deposited at different temperatures. This indicates that the relaxation processes occur through different paths. Most

remarkable example is that of the sample deposited at 82 K. The gauche mole fraction of this sample almost remained at the initial value at deposition in spite of the temperature elevation. This is related to the stable local packing of molecules formed during the deposition at a mild temperature condition. Further discussion will be given at the poster presentation.

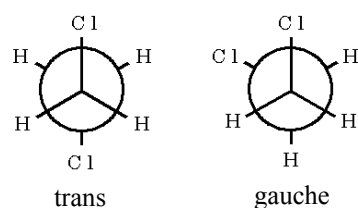


Fig. 1 Conformation isomers of DCE.

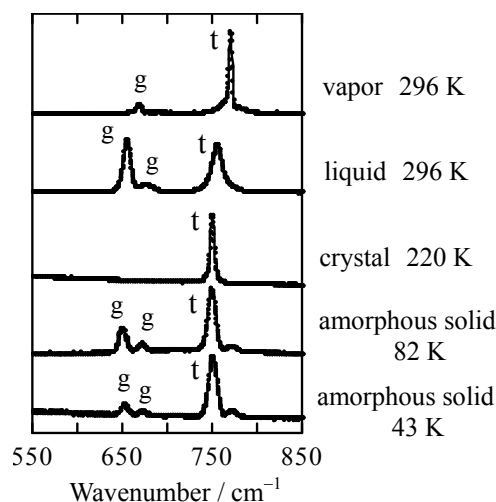


Fig. 2 Raman spectra of DCE in different states.

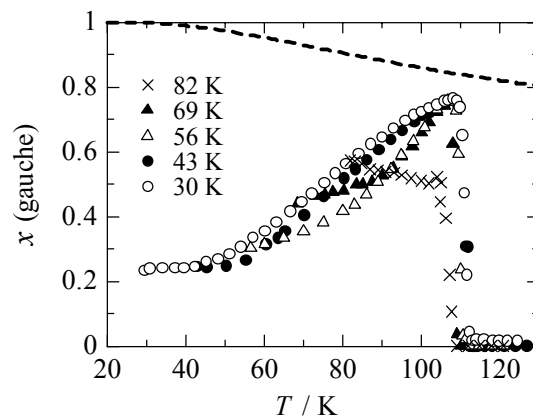


Fig. 3 Evolution of the mole fraction of gauche isomer in amorphous DCE deposited at different temperatures indicated in the figure. Dashed line is the data estimated for supercooled liquid.