有機超薄膜中の超高速スペクトル拡散ダイナミクス

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Ultrafast spectral diffusion dynamics of molecular excitons in ultrathin organic films
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Spectral diffusion immediately after photoexcitation reflects the vibronic coupling in the photoexcited system. In this work, we study spectral diffusion of molecular excitons in thin films of tetracene [1] and 3,4,9,10-perylenetetracarboxylic-diimide (PTCDI) [2] by using two-dimensional electronic spectroscopy (2DES). The samples were prepared in ultrahigh vacuum (UHV) chamber by thermal depositions of the molecules on graphene and measurements have been carried out under the UHV condition. Temperature dependence of the spectral diffusion is studied from 96 to 471 K by analyzing the 2DES signal. Significant acceleration of spectral diffusion with increasing the temperature is observed which cannot be explained by a linear system-bath coupling model with a harmonic bath. We propose an anharmonic coupling model in which the exciton energy gap fluctuations by a high-frequency intramolecular vibration are enhanced by the coupling with a low-frequency phonon mode.

Keywords : Exciton; Two-dimensional electronic spectroscopy; Organic thin film

有機固体中の励起子において，光励起直後にフェムトからピコ秒で進行する超高速スペクトル拡散には熱浴との振電結合が反映されている．本研究では二次元電子分光法(2DES)を超高真空下（$<3.0\times10^{-8}$ Pa）の Graphene/Ir(111)基板上に作製したテトラセンおよび PTCDI の薄膜に適用し，励起子スペクトル拡散挙動を調べた．Fig. 1 および Fig. 2 に示す 2DES 信号の温度依存性から，スペクトル拡散が温度上昇によって加速していることがわかった．この加速を引き起こす機構としては高周波数振動モードと低周波数振動モード間の非調和結合が考えられる．

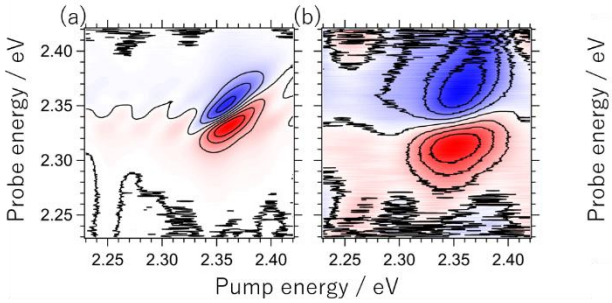

Fig. 1 2DES spectra of tetracene thin films at (a) 96 K and (b)186 K. The delay times are 200 fs.

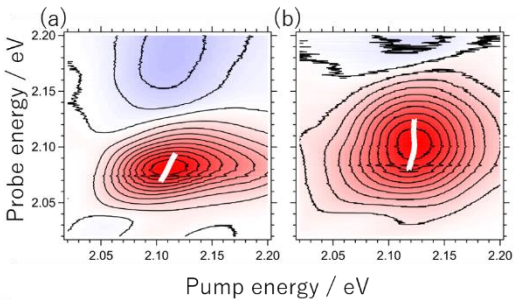

Fig. 2 2DES spectra of PTCDI thin films at (a) 105 K and (b)298 K. The Delay times are 200 fs.

[1] T. Yoshida, K. Watanabe, M. Petrović, M. Kralj, *J. Phys. Chem. Lett.*, **11**, 5248 (2020).
[2] T. Yoshida, K. Watanabe, *J. Phys. Chem. B.*, **125**, 9350 (2021).