

DOUBLE-RESONANCE FACILITATED DECOMPOSITION OF EMISSION SPECTRA

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Emission spectra provide us with rich information about the excited-state processes such as proton-transfer, charge-transfer and so on. In the cases that more than one excited states are involved, emission spectra from different excited states sometimes overlap and a decomposition of the overlapped spectra is desired. One of the methods to perform a decomposition is a time-resolved fluorescence technique. It uses a difference in time evolutions of components involved. However, in the gas-phase, a concentration of the sample is frequently too small to carry out this method. On the other hand, double-resonance technique is a very powerful tool to discriminate or identify a common species in the spectra in the gas-phase. Thus, in the present study, we applied the double-resonance technique to resolve the overlapped emission spectra. When transient IR absorption spectra of the excited state are available, we can label the population of the certain species by the IR excitation with a proper selection of the IR wavenumbers. Thus, we can obtain the emission spectra of labeled species by subtracting the emission spectra with IR labeling from that without IR.

In the present study, we chose the charge-transfer emission spectra of cyanophenyldisilane (CPDS) as a test system. One of us reported that two charge-transfer (CT) states are involved in the intramolecular charge-transfer (ICT) process of CPDS-water cluster and recorded the transient IR spectra^a. As expected, we have succeeded in resolving the CT emission spectra of CPDS-water cluster by the double resonance facilitated decomposition technique. In the present paper, we will report the details of the experimental scheme and the results of the decomposition of the emission spectra.

^aH. Ishikawa, *et al.*, *Chem. Phys. Phys. Chem.*, **9**, 117 (2007).