

## III-J High-Resolution Spectroscopy and Excited-State Dynamics of Jet-Cooled Molecules

The energy structures in the electronic excited states of isolated molecules are of great importance. The excited-state dynamics such as internal conversion to the ground state (IC), intersystem crossing to the triplet state (ISC), intramolecular vibrational redistribution (IVR), vibronic interaction, and predissociation are closely related with the irregular changes of the energy levels, *i.e.*, perturbations. High-resolution laser spectroscopy is one of the powerful methods to investigate the perturbation between the electronic states. The aims of this project are to accurately observe the fluorescence and phosphorescence excitation spectra in a supersonic jet and rotationally resolved spectra of isolated molecules using a new system of coherent narrowband pulse laser light.

In aromatic hydrocarbons such as benzene, naphthalene, and anthracene, the ISC is not expected to be a major process. In contrast with this, the triplet state plays an important role in molecules with the  $n\pi^*$  lowest state such as aldehydes and ketones. The dynamical processes can be understood by analyzing rovibronic structure in the high-resolution spectrum.

### III-J-1 Vibronic Structure in the $S_1$ - $S_0$ Transition of Jet-Cooled Dibenzofuran

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Dibenzofuran is one of the prototypical molecules of toxic dioxins.<sup>1)</sup> We have observed the fluorescence excitation spectrum and dispersed fluorescence spectrum of the  $S_1$ - $S_0$  transition of jet-cooled dibenzofuran. We observed strong vibronic bands whose intensities are larger than the 0–0 band. The observed vibronic bands were assigned referring to *ab initio* calculations of the normal vibrations. The molecule is essentially planar and the structure is not much changed by the electronic excitation. It is concluded that intensities of the observed strong vibronic bands arise from vibronic interaction between the  $S_1$   $^1A_1$  and  $S_2$   $^1B_2$   $\pi\pi^*$  states. The energies of  $b_2$  vibrational bands are decreased by the vibronic interaction. Broad component was observed in the dispersed fluorescence spectrum. It indicates that IVR occurs in the lower energy vibronic levels of the  $S_1$  state.

#### Reference

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### III-J-2 Energy Levels of $CH_3$ Rotation in the $S_1$ and $S_0$ States of 9-Methylanthracene

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$CH_3$  internal rotation induces radiationless transitions of aromatic molecules. In order to understand the mechanism of excited-state dynamics of methyl containing molecules we have observed high-resolution spectra of jet-cooled 9-methylanthracene (9MA). We found several low energy bands, which are assigned to transitions between the vibrational levels of  $CH_3$  internal rotation. The barrier height to  $CH_3$  rotation was estimated to be

about 100 and 50  $cm^{-1}$  in the  $S_0$  and  $S_1$  states, respectively. The barrier height is attributed to steric repulsion and interaction with the  $\pi$  orbitals. The barrier height is very small in toluene and that in 9MA is relatively larger. This increase is considered to be due to larger anisotropy of the  $\pi$  orbitals in 9MA.

The dispersed fluorescence spectra indicate that IVR occurs in the lower energy vibrational levels of the  $S_1$  state. The threshold is much smaller than that of anthracene. The IVR is considered to be enhanced by  $CH_3$  substitution. It is the effect of increase of the level density, lowering of the symmetry, and coupling of the out-of-plane vibrations.

### III-J-3 High-Resolution Spectroscopy of the $T_1$ $^3A_u(n\pi^*)$ State of Oxalyl Chloride

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Oxalyl Chloride is a Cl derivative of glyoxal which is a prototypical diketones. Generally energy difference between the  $n\pi^*$  and  $\pi\pi^*$  states are very small in diketones and ISC occurs efficiently in the  $S_1$  state. The energy structure of the triplet state is an important factor to quantitatively understand the mechanism. In order to observe high-resolution spectrum, strong pulse laser light is necessary because the S–T transition is very weak. In particular Cl atoms enhance radiationless transitions which are called as heavy atom effect. Furthermore, there are two mass isotopes of the Cl atom and the spectrum becomes congested.

Phosphorescence of jet-cooled oxalyl chloride was observed and an S–T phosphorescence excitation spectrum has been reported using a pulse laser with the resolution of 0.2  $cm^{-1}$ .<sup>1)</sup> Pulse amplifying of CW single-mode laser makes it possible to observe rotationally resolved spectrum. The three spin sublevels in the triplet state and the coupling with the rotation angular momentum are important to understand the mechanism of ISC.

#### Reference

1) T. Yoshii *et al.*, *J. Phys. Chem.* **100**, 3354–3358 (1996).