STRUCTURE AND EXCITED-STATE DYNAMICS OF PERYLENE : ULTRAHIGH-RESOLUTION SPECTROSCOPY AND AB INITIO CALCULATION

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Perylene is one of the prototypical compact polycyclic aromatic hydrocarbons (PAHs). The fluorescence quantum yield in the S_1 state is considerably high. It is strange because radiationless transitions such as intersystem crossing (ISC) to the triplet state and internal conversion (IC) to the S_0 state are expected to be fast due to high density of coupling levels. We observed the ultrahigh-resolution spectrum of the S_1 $^1B_{2u} \leftarrow S_0$ ^1A_g transition of jet-cooled perylene, and determined the rotational constants in these two states. [a] The inertial defect is positive and small, so that the molecule is considered to be planar with D_{2h} symmetry. The obtained rotational constants of the S_1 state is very similar to those of the S_0 state. It indicates that the structural change upon electronic transition is very small. We performed $ab\ initio$ calculation, and the calculated geometrical molecular structure and vibrational energies were in good coincidence with the experimental results. The observed high fluorescence quantum yield shows that radiationless transitions are all slow in the S_1 state of perylene. The slow IC can be attributed to the small scale of its structural change. We also observed the ultrahigh-resolution spectrum in the magnetic field of 0.5 Tesla. Zeeman broadening was very small, indicating that the singlet-triplet interaction is very weak, and that ISC is minor in the S_1 state. In specific vibronic levels, the fluorescence lifetimes are remarkably short. We conclude that the main process is IC, and the accepting mode is in-plane (a_g) deformation vibration in the S_1 state.

[a] Y. Kowaka, *et al.*, *J. Mol. Spectrosc.*, **260**, 72 (2010)