VIBRATIONAL AND ROTATIONAL STRUCTURE AND EXCITED-STATE DYNAMICS OF PYRENE

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Pyrene is one of the prototypical compact polycyclic aromatic hydrocarbons (PAHs), and It is important to investigate its molecular structure precisely, because it does not conform to Hückel's $4n+2$ rule. We analyzed high-resolution and ultrahigh-resolution spectra of jet-cooled pyrene and elucidated the vibrational and rotational structures in the S_0 ^1A_g and S_1 $^1B_{3u}$ states. [a] We conclude that the molecule is planar with D_{2h} symmetry. The rotational constants and vibrational normal energies are very similar for the S_0 and S_1 states, indicating that its geometrical structure and potential energy curves are not changed much upon electronic excitation. This small change is common to large PAH molecules because the changes of bond orders by one electron excitation is diluted with a large number of π electrons. The rates of Radiationless transitions in the S_1 state are closely related with the molecular structure and the potential energy curves. Intersystem crossing (ISC) to the triplet state is expected to be very slow in planar PAHs. Internal conversion (IC) to the S_0 state does not occur, if the molecular structure and potential energy curves are identical for the S_0 and S_1 states. In perylene, the fluorescence lifetime is 1400 ns, and the fluorescence quantum yield is considerably high. These properties are attributed to its small changes in molecular structure and potential energy curves upon $S_1 \leftarrow S_0$ excitation.

[a] M. Baba, Y. Kowaka *et al.*, *J. Chem. Phys.*, **131**, 224318 (2009)