

## VIBRATIONAL AND ROTATIONAL STRUCTURE AND EXCITED-STATE DYNAMICS OF PYRENE

YASUYUKI KOWAKA, NOLITAKA ASHIZAWA, MASAACKI BABA, *Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.*

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. <sup>a</sup> 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  $\pi$  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.

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<sup>a</sup>M. Baba, Y. Kowaka *et al.*, *J. Chem. Phys.*, **131**, 224318 (2009)