SPECTRAL DISSIMILARITIES BETWEEN AZULENE($C_{10}H_8$) AND NAPHTHALENE($C_{10}H_8$)

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Polycyclic aromatic hydrocarbons (PAHs) are of great interest in the molecular structure and excited-state dynamics, and there have been extensive spectroscopic and theoretical studies. Azulene and naphthalene are bicyclic aromatic hydrocarbons composed of odd- and even-membered rings, respectively. First, they were discriminated by a theory of mutual polarizability. [a] Naphthalene is an alternant hydrocarbon, but azulene is not. In contrast, spectral resemblances were found by John Platt *et al.*, [b] and were explained by their simple model of molecular orbital. However, the absorption and emission feature of the $S_1$ and $S_2$ states is completely different each other. We have investigated each rotational and vibrational structures, and radiative and nonradiative processes by means of high-resolution spectroscopy [c] [d] and *ab initio* calculation. The equilibrium structures in the $S_0$, $S_1$, and $S_2$ states are similar. This small structural change upon electronic excitation is common to PAH molecules composed of six-membered rings. The fluorescence quantum yield is high because radiationless transitions such as intersystem crossing (ISC) to the triplet state and internal conversion (IC) to the $S_0$ state are very slow in the $S_1$ state. In contrast, the $S_1$ state of azulene is nonfluorescent and the $S_1 \leftarrow S_0$ excitation energy is abnormally small. We consider that the potential energy curve of a $b_2$ vibration is shallower in the $S_1$ state, and therefore the vibronic coupling with the $S_0$ state is strong to enhance the IC process remarkably. This situation is, of course, due to its peculiar characteristics of odd-membered rings and molecular symmetry, which are completely different from the naphthalene molecule.

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[c] Y. Semba, M. Baba, *et al.*, *J. Chem. Phys.*, **131**, 024303 (2009)
[d] K. Yoshida, M. Baba, *et al.*, *J. Chem. Phys.*, **130**, 194304 (2009)