

SPECTRAL DISSIMILARITIES BETWEEN AZULENE(C₁₀H₈) AND NAPHTHALENE(C₁₀H₈)

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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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