STRUCTURE AND RADIATIONLESS TRANSITION OF PAHS : ULTRAHIGH-RESOLUTION SPECTROSCOPY AND AB INITIO CALCULATION

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Polycyclic aromatic hydrocarbons (PAHs) are fascinating objects of basic studies on molecular structure and excited-state dynamics. We have observed and analyzed rotationally resolved ultrahigh-resolution spectra of the $S_1 \leftarrow S_0$ transition of naphthalene, anthracene, pyrene and perylene (all D_{2h} symmetry) in collimated supersonic jets. We conclude that radiationless transitions are all slow in the S_1 zero-vibrational level of the isolated PAH molecule. Possible radiationless processes are intersystem crossing (ISC), internal conversion (IC), and predissociation. [a] Predissociation does not take place because all of the bond energies are larger than the $S_1 \leftarrow S_0$ excitation energy. The observed radiationless process has been presumed to be ISC so far. However, it is inconsistent with El-Sayed's rule that spin-orbit interaction is very weak between the ${}^1\pi\pi^*$ and ${}^3\pi\pi^*$ states. [b] We have observed Zeeman splitting of each rotational line and shown that the magnetic moment is very small in the S_1 state. Therefore, the main radiationless process is not ISC to the triplet state, but IC to the hot ground state. IC is caused by non-Born-Oppenheimer vibronic interaction, [c] which is expected to be very weak if the molecular structure is identical for both electronic states. The experimentally determined rotational constants are almost identical for the S_0 and S_1 states. It is consistent with the observed long lifetime and high fluorescence quantum yield of PAHs. We carried out $ab\ initio$ calculation, and the resultant values of rotational constants of the S_0 state are in extremely good coincidence with the experimental ones for naphthalene and anthracene. On the contrary, for the excited state, it is necessary to perform huge SAC-CI calculation to obtain satisfactory results. Fast IC has been found, for instance, in high vibrational levels of benzene (channel 3), which is due to unavoided potential crossing (conical intersection). However, it is not likely in large PAHs because of the small geometrical change upon electronic excitation, which has been revealed by accurate determination of rotational constants.

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[b] M. El-Sayed, *J. Chem. Phys.*, **38**, 2834 (1963)
[c] S. H. Lin, *J. Chem. Phys.*, **44**, 3759 (1965)