

HIGH-RESOLUTION LASER SPECTROSCOPY AND THE ZEEMAN EFFECT: DIBENZOTHIOPHENE

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For planar aromatic hydrocarbons, intersystem crossing to the triplet state is expected to be very slow according to El Sayed's rule^{ab}. The fluorescence lifetime in the S_1 state of dibenzothiophene is remarkably shorter compared with the analogous molecules such as dibenzofuran. Pratt et al. suggested that the main fast process was intersystem crossing on the basis of the result of high-resolution laser spectroscopy^c. We observed the high-resolution spectrum in the external magnetic field in order to confirm the contribution of the triplet state. However, no change has been found in the spectrum up to 1.0 Tesla, indicating that the intersystem crossing is slow and is not the main process for the fluorescence decay in the S_1 state of dibenzothiophene. It should be noted that the spectral feature of the $S_1 \leftarrow S_0$ 0_0^0 band of dibenzothiophene is *b*-type, whereas that of dibenzofuran is *a*-type. The relatively faster decay is considered to be the result of different character in the S_1 electronic state. Several electronic excited states are expected to be located in the lower energy region^d. Ab initio theoretical calculation of B3LYP/6-311G+(2d,p) accurately reproduced the experimental values of rotational constants and excitation energy. The S_1 state has been assigned to 1A_1 , which is consistent with the fact that the $S_1 \leftarrow S_0$ transition is *b*-type.

^aM. Baba, N. Nakayama, et al., *J. Chem. Phys.* **130**, 134315 (2009).

^bM. Baba, *J. Phys. Chem. A* **115**, 9514 (2011).

^cL. Alvarez-Valtierra, John T. Yi, and David W. Pratt, *J. Phys. Chem. A* **113**, 2261(1990).

^dM. Baba, T. Katori, M. Kawabata, S. Kunishige, and T. Yamanaka, *J. Phys. Chem. A* **117**, 13524 (2013).