ULTRAHIGH-RESOLUTION SPECTROSCOPY IN THE ”CHANNEL THREE” REGION OF BENZENE

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Dynamical processes in the excited state of benzene is of great interest and the ultrahigh-resolution spectroscopy is powerful to investigate them quantitatively. The fluorescence quantum yield drastically decreases in the vibrational levels above 3000 cm^{-1} of the S$_1$ $^1B_{2u}$ state, so called ”channel three” region. It was concluded by Riedle and Neusser that this phenomenon originates from intramolecular vibrational redistribution (IVR). [a] We have observed the ultrahigh-resolution spectrum of the S$_1$ $^1B_{2u} \leftarrow$ S$_0$ $14^1_0 1^2_0$ band. [b] The vibrational energy of the upper level is 3412 cm^{-1}. The rotational lines are washed out except $K = 0$ lines at low J and $K = J$ lines at high J. It is caused by the lifetime broadening due to Coriolis interactions with other vibrational levels. We also observed the change of the spectrum with the magnetic field. The Zeeman splitting was found to be large for the $K = J$ levels, but the amplitude was still much smaller than that expected by the interaction with the triplet state. It is concluded that the magnetic moment originates from the electronic orbital angular momentum arising from a mixing of the S$_1$ $^1B_{2u}$ and S$_2$ $^1B_{1u}$ states via $J - L$ coupling. The intersystem crossing (ISC) is found not to be an important process even in the ”channel three” region.

[a] E. Riedle and H. J. Neusser, *J. Chem. Phys.*, **89**, 4620 (1988).

[b] D. Y. Baek, J. Chen, J. Wang, A. Doi, S. Kasahara, M. Baba, and H. Katô *Bull. Chem. Soc. Jpn.*, **79**, 75 (2006).