

DOPPLER-FREE TWO-PHOTON ABSORPTION SPECTROSCOPY AND THE ZEEMAN EFFECT OF BENZENE

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A Doppler-free absorption spectrum and the Zeeman effect of the $A^1B_{2u} \leftarrow X^1A_{1g}$ transition of benzene have been measured by means of two-photon absorption spectroscopy within an external cavity. Rotational lines were fully resolved and the accurate molecular constants have been determined for the $A^1B_{2u}(v_{14} = 1, v_1 = 1)$ state. The Zeeman splittings for lines of a given J were observed to increase regularly with K and reach a maximum at $K = J$. This demonstrates that the magnetic moment lies along the c axis (perpendicular to the molecular plane). The magnetic moment of the $A^1B_{2u}(v_{14} = 1, v_1 = 1, J = 43, K = 43)$ level was determined to be $0.005 \mu_B$. The Zeeman splittings of the $K = J$ levels were observed to increase with increasing J . It is concluded that the $S_1^1B_{2u}$ state is mixed with the $^3E_{2u}(\sigma, \pi^*$ or $\sigma^*, \pi)$ state. The $^1B_{2u}(S_1) \rightarrow ^3B_{1u}(T_1)$ and $^1B_{2u}(S_1) \rightarrow ^3E_{1u}(T_2)$ intersystem crossings are suggested to occur through the vibronic interactions between $^3E_{2u}$ and $^3B_{1u}(T_1)$ and between $^3E_{2u}$ and $^3E_{1u}(T_2)$ through the mixed $^3E_{2u}$ component, respectively, and the spin-orbit interaction between the the $S_1^1B_{2u}$ and $^3E_{2u}(\sigma, \pi^*$ or $\sigma^*, \pi)$ states.^a

^aM. Misono, J. G. Wang, M. Ushino, M. Okubo, H. Katô, M. Baba, and S. Nagakura, *J. Chem. Phys.*, **116**, 162 (2002).