Jet Spectroscopy of the D_1 $\mathbf{2}^2B_1$ – D_0 $\mathbf{1}^2B_1$ Electronic Transition of the p-Cyanobenzyl Radical

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We have generated the p-cyanobenzyl radical in supersonic free expansion, and measured the laser induced fluorescence (LIF) spectra in green-blue region; the vibrationally and rotationally resolved LIF excitation spectra and the LIF dispersed spectra from the single vibronic levels (SVL). On the basis of the vibronic structures in the SVL dispersed spectra, the lowest energy band at 20735 cm^{-1} with the strongest intensity in the excitation spectrum has been assigned to the 0_0^0 band of the visible spectrum. Based on the band type of the 0_0^0 band, a-type, determined from the rotationally resolved LIF excitation spectrum, we have definitely assigned the visible band to the D_1 2^2B_1 – D_0 1^2B_1 electronic transition. We have found on the grounds of the vibrational analysis of the dispersed spectra, that the vibronic structure of the 2^2B_1 – 1^2B_1 electronic transition of the benzyl type was characterized by totally symmetric fundamental modes, 1, 8a, and 9a, with the frequencies higher than 800 cm^{-1}, while those of the 1^2A_2 – 1^2B_1 electronic transition are non-totally symmetric modes, 6b and 8b, and totally symmetric modes, 6a and 1, with the frequencies lower than 800 cm^{-1} [a].

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[a] M. Fukushima, K. Obi, Chem. Phys. Lett. **248**, 269 (1996)