LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE C_4H AND C_4D RADICALS

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Laser-induced-fluorescence spectra of the C_4H and C_4D radicals have been observed for the first time. The molecules were generated in a supersonic jet by an electric discharge of C_2H_2 or C_2D_2 diluted in Ar. Fourteen and thirteen vibronic bands were observed for C_4H and C_4D respectively, in the near UV region(24000 - 25000 cm^{-1}). The bands were assigned to the $^2\Sigma$-$^2\Sigma$ or $^2\Pi$-$^2\Sigma$ type, and several $^2\Sigma$-$^2\Sigma$ bands were subjected to rotational analyses. The determined rotational constants for the lower state agree with those for C_4H/C_4D in the ground vibrational level in the $X^2\Sigma$ state, which were reported in a previous microwave study [a] [b]. The spin-orbit splittings in the $^2\Pi$-$^2\Sigma$ bands are 16 and 12 cm^{-1} for C_4H and C_4D, respectively, leading a conclusion that the excited electronic state for the observed band system is $^2\Pi$. The present observation is consistent with a recent CASSCF study[c], which predicted the $B^2\Pi$ state with the excitation energy of 24500 cm^{-1}.

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[c]A.L. Sobolewski and L. Adamowicz, J. Chem. Phys. 102, 394 (1995).