ROTATIONAL SPECTRA OF THE H_2-HCN COMPLEX OBSERVED BY FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY. THE INTERNAL ROTATION OF H_2 IN THE H_2-HCN COMPLEX.

M. ISHIGURO, K. HARADA, KEIICHI TANAKA AND T. TANAKA, *Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, 812-8581 Japan*; Y. SUMIYOSHI AND Y. ENDO, *Department of Pure and Applied Sciences, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguroku, Tokyo, 153-8902, Japan*.

Fourier-Transform Microwave (FTMW) spectroscopy has been applied to the observation of the $J = 1 - 0$ rotational lines of the H_2-HCN and H_2-DCN complexes for the $ortho$- and $para$-H_2 species. The rotational constants derived for the HCN/DCN complexes support definitely that H_2 is attached to the N end of HCN for the $ortho$-H_2 species, while H_2 is attached to the H end of HCN for the $para$-H_2 species, consistent with the recent vibrational spectra in the He-droplet [a]. The nuclear quadrupole interaction constants of the nitrogen nucleus ($I_N = 1$) show that the HCN/DCN part executes a floppy motion with a large mean amplitude.
The splitting due to the magnetic hyperfine interaction of the H_2 part was observed for ortho-H_2-HCN ($j = 1$ for H_2 internal rotation) thanks to the high resolution of FTMW spectroscopy, but not for para-H_2-HCN ($j = 0$ for H_2 internal rotation). Because of Σ symmetry of the ortho-H_2-HCN complex in the ground state, nuclear spin-nuclear spin interaction contributes to the hydrogen hyperfine interaction, but not the nuclear spin-rotation intraction. The magnetic interaction constant d_H for ortho-H_2-HCN was determined to be 54.6(38) kHz. The value corresponds to 94.7% of that of free hydrogen molecule 57.671(24) kHz [b], indicating almost free rotation of the H_2 part in the complex. The spectrum of ortho-H_2-DCN shows also the splitting due to the magnatic hyperfine interaction of H_2, but the hyperfine partern is more complicated because of the nuclear quadrupole interaction of the D atom ($I_D = 1$). The magnetic interaction constant for ortho-H_2-DCN indicates that H_2 is rotating almost freely in the complex as well.

[a] D. T .Moore, M. Ishiguro, and R. E. Miller, *J. Chem. Phys.* 115, 5144 (2001)
[b] H. G. Kolsky and N. F. Ramsey, *Phys. Rev.* 87, 395 (1952)