SPECTROSCOPY AND VIBRATIONAL PREDISSOCIATION OF Ar_nHF AT v_{HF}=3

CHENG-CHI CHUANG, SUSY N. TSANG, JASON HANSON and WILLIAM KLEMPERER, *Department of Chemistry, Harvard University, Cambridge, MA 02138*; HUAN-CHNEG CHANG, *Institute of Atomic and Molecular Sciences, Academica Sinica, P.O.Box 23-166, Taipei, Taiwan 10764, Republic of China*.

Second overtone spectra of Ar_nHF (n=1,2 and 3) are observed by intracavity laser induced fluorescence. For ArHF(3000) the fluorescence radiation is dispersed and the rotational distribution of the HF (v=2) fragments are measured. The high intensity of fluorescence radiation is mainly due to the emission (v=3→1) of the undissociated ArHF, which indicates the lifetime of the (3000) state is significantly long, $\approx 2\times10^{-5}$ sec. Additional new bend-stretch combination state of ArHF(3111) has been observed by both (3111)←(0100) hot band and (3111)←(0000) direct excitations. The preliminary spectroscopic constants of the (3111) are 11455.932 cm^{-1} and B=0.08490 cm^{-1} thus placing this state 116.898 cm^{-1} above the fundamental (3000). For Ar_2HF, four states correlating with j=0 and j=1 of HF(v=3) have been observed. The spectroscopic constants of these four bands are summarized as follows:

	ν_0(band origin)	$\Delta\nu$	A	B	C
Σ_0	11323.783	-49.03	0.12023	0.05830	0.03894
Π_{in}	11387.730	63.95	0.12267	0.05705	0.03842
Π_{out}	11426.811	102.03	0.12026	0.05812	0.03863
Σ_1	11427.480	103.69	0.12026	0.05813	0.03764

The results provide direct probe of the three-body (non-additive) forces and are compared with the theoretical model of Ernesti and Hutson.[a] For Ar_3HF the rovibrational lines of the v_{HF}=3 fundamental stretch state (ν_0=11310.451 cm^{-1}; 62 cm^{-1} red shift) are fitted by Voigt profile with Doppler and Lorenztian components of 100(10) and 50(10) MHz, respectively. The 50(10) MHz Lorenztian linewidths are attributed to the vibrational predissociation broadening (3 nsec in lifetime) for Ar_3HF at v_{HF}=3.

[a] A. Ernesti and J. M. Hutson, *Phys. Rev.* A**51**, 239 (1995).