THE DEPENDENCE OF INTERMOLECULAR INTERACTIONS UPON VALENCE COORDINATE EXCITATION: THE v_{HF}=4 LEVELS OF ArHF

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The valence state dependence of the Ar−HF interaction potential is extended to $v_{HF} = 4$. Three new ArHF ($v_{HF} = 4$) states, (4000), (4100), and (4110), are observed between 14780 and 14880 cm^{-1} using intracavity laser induced fluorescence. The spectroscopic constants of these states are: (4000) ν_0 = 14783.60323(30) cm^{-1}, and B = 0.1036068(68) cm^{-1}; (4100) ν_0 = 14867.41906(70) cm^{-1}, B = 0.102612(27) cm^{-1}; and (4110) ν_0 =14875.04673(31) cm^{-1}, B = 0.1012823(73) cm^{-1} respectively. In conjunction with the previous ArHF results (v_{HF}=0−3), the spectral red shifts of ArHF(v000) increase more rapidly than linearly, from 9.654 cm^{-1} at v=1 to 48.024 cm^{-1} at v=4. The rotational constants of ArHF(v000) increase essentially linearly with v_{HF}, noticeably increased by 1.30 % (40 MHz) at v=4. The classical turning point of HF is extended by 0.4 Å from r_e at v=4, showing no evidence for Ar−H repulsion. The spectral red shift for linear hydrogen bonded Ar−HF (v000) indicates a strong enhancement of binding energy upon HF valence bond elongation, while the rotational constant indicate an almost surprising decrease in heavy atom separation. Both the T-shaped ArHF(v110) and anti-linear Ar−FH(v100), however, show very little dependence of binding energy upon v_{HF} valence excitation. These observations are in good accord with the *ab initio* calculations of the Ar−HF intermolecular potential surface.