

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  $\text{cm}^{-1}$  using intracavity laser induced fluorescence. The spectroscopic constants of these states are: (4000)  $\nu_0 = 14783.60323(30) \text{ cm}^{-1}$ , and  $B = 0.1036068(68) \text{ cm}^{-1}$ ; (4100)  $\nu_0 = 14867.41906(70) \text{ cm}^{-1}$ ,  $B = 0.102612(27) \text{ cm}^{-1}$ ; and (4110)  $\nu_0 = 14875.04673(31) \text{ cm}^{-1}$ ,  $B = 0.1012823(73) \text{ cm}^{-1}$  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  $\text{cm}^{-1}$  at  $v=1$  to 48.024  $\text{cm}^{-1}$  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.