INTRAMOLECULAR DYNAMICS OF THE $N = 2$ HF STRETCHING OVERTONE POLYAD OF $(HF)_2$ STUDIED BY HIGH-RESOLUTION cw-DIODE LASER CAVITY RING-DOWN SPECTROSCOPY IN A PULSED SLIT JET

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The $(HF)_2$ hydrogen bonded dimer has been a prototype system for high-resolution spectroscopy since the pioneering studies of its microwave spectra by Dyke, Howard, and Klemperer in 1972.[1] Subsequently the HF stretching fundamentals were studied in 1983,[2] a low frequency fundamental analyzed in the far infrared in 1987,[3] HF stretching overtone spectra investigated by FTIR spectroscopy[4] and finally full dimensional potential energy hypersurfaces developed of near to spectroscopic accuracy.[5,6] All these were "first" achievements prototypical for any type of hydrogen bonded dimer of this kind. Here we present the first study of the $N = 2$ HF stretching overtone polyad by very high resolution cw-diode laser cavity ring-down spectroscopy in pulsed slit jet expansions developed recently[7] (instrumental bandwidth about 1 MHz corresponding to a resolving power of 2×10^8). An analysis of all polyad subbands in terms of spectroscopic constants, tunneling splittings, Lorentzian predissociation and Doppler contributions to the linewidths will be presented.[8] The results agree well with full six-dimensional calculations[9] but disagree with simple models or approximate calculations that have been presented in the past.

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