

## JET SPECTROSCOPY OF THE $\nu_4$ BAND OF HYDROGEN FLUORIDE TETRAMER IN THE 714 $\text{cm}^{-1}$ REGION

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Using our slit-jet, infrared diode laser spectrometer, we have observed a rotationally resolved parallel band centered at 714  $\text{cm}^{-1}$  in a pulsed molecular beam formed by expanding a mixture of 4% HF in helium through a 200  $\mu\text{m}$  x 12 cm slit with a backing pressure of ca. 1000 Torr. A set of excited and ground state spectroscopic constants were fit simultaneously to a data set of 204 transitions using a symmetric top, semi-rigid rotor Hamiltonian. The fit constants are  $\nu_0 = 714.7849(1) \text{ cm}^{-1}$ ,  $B' = 0.129614(5) \text{ cm}^{-1}$ ,  $(C' - B') - (C'' - B'') = 0.001339(6) \text{ cm}^{-1}$ ,  $D'_J = 4.9(2) \times 10^{-7} \text{ cm}^{-1}$ ,  $D'_{JK} = -1.1(2) \times 10^{-6} \text{ cm}^{-1}$ ,  $D'_K - D''_K = -2.81(8) \times 10^{-6} \text{ cm}^{-1}$ ,  $H'_{JKK} = -2.0(2) \times 10^{-8} \text{ cm}^{-1}$ ,  $H'_{KKK} - H''_{KKK} = -4.68(6) \times 10^{-8} \text{ cm}^{-1}$ ,  $B'' = 0.132059(5) \text{ cm}^{-1}$ ,  $D''_J = 5.1(2) \times 10^{-7} \text{ cm}^{-1}$ ,  $D''_{JK} = -1.3(2) \times 10^{-6} \text{ cm}^{-1}$ ,  $H''_{JKK} = -6(2) \times 10^{-9} \text{ cm}^{-1}$ , and the RMS deviation of the obs - calcs is 0.00045  $\text{cm}^{-1}$ . We have also observed two other bands in the 700 to 775  $\text{cm}^{-1}$  region: one band is a strongly perturbed perpendicular band centered at 752  $\text{cm}^{-1}$  with  $B'' = 0.133 \text{ cm}^{-1}$  and the other band is a perturbed parallel band centered at 741  $\text{cm}^{-1}$  with  $B'' = 0.0755 \text{ cm}^{-1}$ . For hydrogen fluoride tetramer and pentamer, theory predicts (Maerker, et al.)<sup>a</sup> planar, oblate symmetric top structures at their global minima with  $B_e$  values of 0.136 and 0.0767  $\text{cm}^{-1}$  for  $(\text{HF})_4$  ( $C_{4h}$  symmetry) and for  $(\text{HF})_5$  ( $C_{5h}$  symmetry), respectively. We have tentatively assigned the 714  $\text{cm}^{-1}$  band as the  $\nu_4$  ( $A_u$ ) HF out-of-plane torsion of the tetramer, the 752  $\text{cm}^{-1}$  band as the  $\nu_{13}$  ( $E_u$ ) HF in-plane torsion of the tetramer, and the 741  $\text{cm}^{-1}$  band as the  $\nu_4$  ( $A''$ ) HF out-of-plane torsion of the pentamer.

<sup>a</sup>C. Maerker, P. R. Schlyer, K. R. Liedl, T. -K. Ha, M. Quack, M. A. Suhm, *J. Comp. Chem.* 18 1695 (1997).