OBSERVATION OF THE a_1 CH STRETCHING MODES OF PHENYL RADICAL

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High resolution spectroscopy for infrared rovibrational transitions in the CH stretching manifold of phenyl radical (C_6H_5) has been investigated in the slit-jet supersonic expansion at sub-Doppler resolution (60 MHz). Two new fundamental modes are observed and analyzed in this present study, corresponding to b-type structure originating from excitation of the fundamentals v_1 and v_2 mode. The band origins are determined to be 3073.96850(8) cm^{-1} and 3062.26480(7) cm^{-1}, respectively, which agree well with theoretical anharmonic scaling prediction within 5 cm^{-1} based on the B3LYP/6-311g++(3df,3dp) basis set, but shifted by 11 cm^{-1} from the corresponding experimental Ar-matrixs results of Ellison and coworkers[a]. Intensities for the three bands are also analyzed, with the relative intensities between these three agreeing well with theoretical calculation. The physical interpretation of the inertia defect and perturbations of the band positions to explain the experimental observation and the frequencies shift.

[a] Anders. V. Friderichsen, Juliusz G. Radziszewski, Mark R. Nimols, Paul R. Winter, David C. Dayton, Donald E. David, and G. Barney Ellison, J. Am. Chem. Soc. 123, 1977 (2001)