THE DISCOVERY OF BRIDGED HPSI BY ROTATIONAL SPECTROSCOPY

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The pure rotational spectrum of bridged HPSi, the isomer calculated to be the global minimum of the [H,Si,P] potential energy surface, has been measured using a combination of Fourier transform microwave spectroscopy (FTM) and millimeter/submillimeter direct absorption techniques. In the centimeter-wave band, the lowest two a-type rotational transitions in the $K_a = 0$ ladder were measured for the normal isotopic species, $HP^{29}Si$, $HP^{30}Si$, and DPSi in a supersonic molecular beam discharge source using a dilute mixture of SiH_4 (or SiD_4) and PH_3. The experimental work was initially guided by theoretical structures and rotational constants obtained at the CCSD(T)/cc-pwCVQZ level of theory and zero-point vibrational corrections at the CCSD(T)/cc-pV(T+*d*)Z level. Following detection of HPSi in the FTM experiment, theoretical best estimates for the structure and the rotational constants were obtained using additivity and extrapolation techniques.

On the basis of the centimeter-wave data, the millimeter/submillimeter spectrum of normal HPSi was subsequently measured between 287 and 421 GHz, including K_a components from K_a = 0 to 5, using a combination of gas-phase elemental phosphorus, H_2, and SiH_4 diluted in argon through an AC glow discharge. From the combined data set, precise spectroscopic constants have been determined using a standard asymmetric top Hamiltonian; all of the measured constants are in excellent agreement with those predicted from theory. From the available data, an unusual H-bridged structure has been derived in which the H atom is situated slightly closer to the P atom. The geometry of HPSi is in remarkable contrast to that of the C and/or N anaogues, i.e. HCN/HNC, HCP, and HNSi which are all linear.