NEW PERSPECTIVE ON PF_n (n=1–5) FROM THE RECOUPLED PAIR BONDING MODEL: A QUANTUM CHEMICAL STUDY

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Structures of the PF_n family (n=1–5) were characterized with high level RCCSD(T) coupled cluster theory calculations using triple and quadruple zeta quality correlation consistent basis sets. In addition to accounting for the well-known ground states of PF through PF_5, insight from the recoupled pair bonding model also led to locating a previously unknown $^3B_1$ state of PF_3, which lies about 90 kcal/mol above $PF_3(^1A_1)$ but is still bound with respect to $PF_2(^2B_1)$+F(^2P) by about 40 kcal/mol. We also revisited the less-studied C_{3v} local minimum on the PF_4 doublet surface and characterized the transition state for interconversion to the C_{2v} global minimum. The energetics suggest that both $PF_3(^3B_1)$ and C_{3v} $PF_4(^2A_1)$ are potentially observable in the laboratory. The trends in the bond dissociation energies and relative energy differences of the PF_n family are very consistent with predictions from the recoupled pair bonding model.