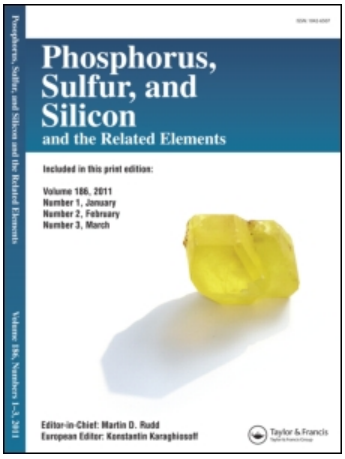

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Vertical Electronic Spectra of the Isovalent Molecules H_2CNH, H_2SiNH, H_2CPH and H_2SiPH on the Basis of MRD-CI Calculations

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To cite this Article Bruna, Pablo J. , Krumbach, Volker and Peyerimhoff, Sigrid D.(1987) 'Vertical Electronic Spectra of the Isovalent Molecules H_2CNH, H_2SiNH, H_2CPH and H_2SiPH on the Basis of MRD-CI Calculations', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 3, 698
To link to this Article: DOI: 10.1080/03086648708079192
URL: http://dx.doi.org/10.1080/03086648708079192

Vertical Electronic Spectra of the Isovalent Molecules H_2CNH, H_2SiNH, H_2CPH and H_2SiPH on the Basis of MRD-CI Calculations

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Large-scale multi-reference single and double-excitation configuration interaction (MRD-CI) calculations are employed for the study of the isovalent compounds H_2CNH, H_2SiNH, H_2CPH and H_2SiPH in their ground state equilibrium geometry. The dipole moments and charge distributions are given. The vertical excitation energies to the intra-valence states $^{3,1}(n, \pi^*)$ and $^{3,1}(\pi, \pi^*)$ and to the first members of the Rydberg series originating from n and π MO's respectively are predicted; the first two ionization potentials and the Rydberg term values are also calculated. In H_2CNH, mixing of Rydberg and valence-shell states with CN stretching is analyzed. The trends in relative stability of electronic and ionized states can be directly related to increased orbital stability of n relative to π as soon as a first-row constituent is replaced by a second-row atom. The calculations explain the diffuse character of the uv spectrum of imines; they treat the molecules H_2SiNH and H_2SiPH for the first time and present a large number of data for all four molecules which can serve as a basis for future experimental investigations on these and related compounds.