

ANALYSIS OF SINGLET AND TRIPLET STRUCTURE IN THE HIGH-RESOLUTION SPECTRUM OF ZIRCONIUM MONOCARBIDE

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ZrC is readily produced in supersonic expansion via reaction of 1% methane (in helium) with laser-ablated zirconium metal. Laser-induced fluorescence excitation and dispersed emission spectra have been recorded for bands in the region 630 – 520 nm (16000 – 19000 cm⁻¹). The four lowest electronic states lie below 2500 cm⁻¹ and appear to represent all possible arrangements of two electrons in the two nearly degenerate 11σ and 12σ orbitals (both formed from Zr 5sσ + C 2pσ); the evidence is that the small spin-spin interaction of the X³Σ⁺ ground state (λ₀ = 0.5142 cm⁻¹, r₀ = 1.807 Å for ⁹⁰Zr¹²C) is consistent with a σσ' configuration, while the anomalous ¹²C/¹³C isotope shifts and vibrational intervals of the remaining three states show that they all have the same (¹Σ⁺) symmetry. In particular, the tightly bound a¹Σ⁺ state (T₀ = 187.83 cm⁻¹, r₀ = 1.739 Å) arises from the 11σ² closed shell configuration. Moreover, this molecular orbital scheme is consistent with the confused level structure above 16000 cm⁻¹. At least four close-lying Π states (two singlets and two triplets) are observed and can be explained by the promotion of either σ electron to a π orbital; these exhibit both isoconfigurational (¹Π/³Π₁) and interconfigurational (¹Π/¹Π or ³Π/³Π) interactions. Details of the rotational and ⁹¹Zr (I = 5/2) hyperfine structures will be presented.

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