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

ANTHONY J. MERER and JAMES R.D. PEERS[a], *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1*; SCOTT J. RIXON, *Department of Physics and Astronomy, University of British Columbia, 6224 Agricultural Road, Vancouver, BC, Canada V6T 1Z1*.

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 $5s\sigma$ + C $2p\sigma$); the evidence is that the small spin-spin interaction of the $X^3\Sigma^+$ ground state ($\lambda_0 = 0.5142$ cm^{-1}, $r_0 = 1.807$ Å for $^{90}Zr^{12}C$) is consistent with a $\sigma\sigma'$ configuration, while the anomalous $^{12}C/^{13}C$ isotope shifts and vibrational intervals of the remaining three states show that they all have the same ($^1\Sigma^+$) symmetry. In particular, the tightly bound $a^1\Sigma^+$ state ($T_0 = 187.83$ cm^{-1}, $r_0 = 1.739$ Å) arises from the $11\sigma^2$ 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 ($^1\Pi/^3\Pi_1$) and interconfigurational ($^1\Pi/^1\Pi$ or $^3\Pi/^3\Pi$) interactions. Details of the rotational and ^{91}Zr ($I = 5/2$) hyperfine structures will be presented.

[a]Present address: Creo Inc., 3755 Willingdon Avenue, Burnaby, BC, Canada V5G 3H3