

THE ROTATIONALLY RESOLVED NEAR INFRARED BAND SYSTEMS OF TiCo AND ZrCo

S. M. SICKAFOOSE, M. D. MORSE, *Department of Chemistry, University of Utah, Salt Lake City, UT 84112*; and D. A. HALES, *Department of Chemistry, Hendrix College, Conway, AR 72032*.

Resonant two-photon ionization spectroscopy has been used to provide the first rotationally resolved work involving multiply-bonded mixed early-late (or Brewer-Engel) transition metal dimers. The mixed metal dimers TiCo and ZrCo are shown to possess $^2\Sigma^+$ ground states, in agreement with previous matrix isolation ESR studies. Two previously observed vibronic bands in ZrCo were rotationally resolved, as was one of several newly discovered vibronic transitions in TiCo. Ground state rotational constants for $^{48}\text{Ti}^{59}\text{Co}$ and $^{90}\text{Zr}^{59}\text{Co}$ were measured to be $B_0'' = 0.18615(8) \text{ cm}^{-1}$ and $B_0'' = 0.11909(7) \text{ cm}^{-1}$, giving $r_0'' = 1.8508(4) \text{ \AA}$ and $r_0'' = 1.9941(6) \text{ \AA}$, respectively. In both molecules the ground state conforms to the Hund's case $b_{\beta S}$ coupling scheme, with Fermi contact interactions between the unpaired σ electron and the ^{59}Co ($I = 7/2$) nucleus of $b_F'' = 0.0468(7) \text{ cm}^{-1}$ for $^{48}\text{Ti}^{59}\text{Co}$ and $b_F'' = 0.0551(7) \text{ cm}^{-1}$ for $^{90}\text{Zr}^{59}\text{Co}$. These values indicate that the unpaired electron occupies a σ orbital having 32% and 37.5% Co 4s character in TiCo and ZrCo, respectively. All three of the rotationally resolved bands are $^2\Pi_{3/2} \leftarrow X^2\Sigma^+$ transitions. For $^{90}\text{Zr}^{59}\text{Co}$ the 0 - 0 and 1 - 0 bands were resolved at $\nu_0 = 10496.1690(44) \text{ cm}^{-1}$ and $10884.4266(24) \text{ cm}^{-1}$, giving $B_0' = 0.11922(8) \text{ cm}^{-1}$ and $B_1' = 0.11962(6) \text{ cm}^{-1}$. For $^{48}\text{Ti}^{59}\text{Co}$ the rotationally resolved band had $\nu_0 = 9873.8342(19) \text{ cm}^{-1}$ and $B' = 0.19107(6) \text{ cm}^{-1}$. These results will be discussed in the context of prior work on these and related molecules.