LASER SPECTROSCOPY AND DENSITY FUNCTIONAL STUDY ON NIOBIUM DIMER CATION

METIN AYDIN, *Department of Chemistry, Faculty of Art and Sciences, Ondokuz Mayis University, 55139, Samsun, Turkey*; JOHN R. LOMBARDI , *Department of Chemistry and Center for Analysis of Structures and Interfaces (CASI), The City College of New York (CCNY), New York, NY10031*.

Resonant multiphoton fragmentation spectra of niobium dimer cation (Nb2+) have been obtained by utilizing laser vaporization of a Nb metal target. Ions are mass-selected with a time-of-flight mass spectrometer followed by a mass gate, then fragmented with a pulsed dye laser, and the resulting fragment ions are detected with a second time-of-flight reflectron mass spectrometer and multichannel plate. Photon resonances are detected by monitoring ion current as a function of fragmentation laser wavelength. A rich, but complex spectrum of the cation is obtained. The bands display a characteristic multiplet structure that may be interpreted as due to transitions from the ground state $X^4\Sigma^-(\Omega g)$ to several excited states, $X^4\Pi(\Omega u)$ and $X^4\Sigma(^-\Omega u)$. The ground state $X^4\Sigma^-(\Omega g)$ is derived from the electron configuration $(\pi_u)^4\ (1\sigma_g)^2(2\sigma_g)^1\ (\delta_g)^2$. The two spin-orbit components are split by 145 cm^{-1} due to a strong second-order isoconfigurational spin-orbit interaction with the low-lying $^2\Sigma^+(\Omega g)$ state. The vibrational frequencies of the ground sate and the excited state of Nb2+ are identified as well as molecular spin-orbit constants (A_{SO}) in the excited state. The electronic structure of niobium dimer cation was investigated using density functional theory. For the electronic ground state, the predicted spectroscopic properties were in good agreement with experiment. Calculations on excited states reveal congested manifolds of quartet and doublet electronic states in the range 0-30,000 cm^{-1}, reflecting the multitude of possible electronic promotions among the 4d- and 5s-based molecular orbitals. Comparisons are drawn between $Nb^+{}_2$ and the prevalent isoelectronic molecules $V^+{}_2$/NbV^+/Nb_2/V_2/NbV.[a]

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