

LASER SPECTROSCOPY AND DENSITY FUNCTIONAL STUDY ON NIOBIUM DIMER CATION

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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 X⁴Σ⁻(Ω_g) to several excited states, X⁴Π(Ω_u) and X⁴Σ⁻(Ω_u). The ground state X⁴Σ⁻(Ω_g) is derived from the electron configuration (π_u)⁴(1σ_g)²(2σ_g)¹(δ_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 ²Σ⁺(Ω_g) state. The vibrational frequencies of the ground state 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 Nb₂⁺ and the prevalent isoelectronic molecules V₂⁺/NbV⁺/Nb₂/V₂/NbV.^a

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