

Electronic transitions of tungsten monosulfide

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Abstract

Electronic transition spectrum of the tungsten monosulfide (WS) molecule in the near infrared region between 725 nm and 885 nm has been recorded using laser ablation/reaction free-jet expansion and laser induced fluorescence spectroscopy. The WS molecule was produced by reacting laser - ablated tungsten atoms with 1% CS₂ seeded in argon. Fifteen vibrational bands with resolved rotational structure have been recorded and analyzed, which were organized into seven electronic transition systems. The ground state has been identified to be the X³Σ⁻(0⁺) state with bond length, r_0 , and vibrational frequency, $\Delta G_{1/2}$, determined to be 2.0676 Å and 556.7 cm⁻¹ respectively. In addition, vibrational bands with $\Omega = 1$ component in lower state have also been analyzed. Least-squares fit of the measured line positions yielded molecular constants for the electronic states involved.

Spectroscopic constants and potential energy curves of 30 low-lying Λ -S states and Ω sub-states of the WS molecule have been calculated using state-averaged complete active space self-consistent field (SA-CASSCF) and followed by MRCISD+Q (internally contracted multi-reference configuration interaction with singles and doubles plus Davidson's cluster correction). The active space consists of 10 electrons in 9 orbitals corresponding to the W 5*d6s* and S 3*p* shells. The lower molecular orbitals from W 5*s5p* and S 3*s* are inactive but are also correlated, and relativistic effective core potential (RECPs) are adopted to replace the core orbitals with 60 (W) and 10 (S) core electrons, respectively. The spin-orbit coupling (SOC) is calculated via the state-interaction (SI) approach with RECP spin-orbit operators using SA-CASSCF wavefunctions, where the diagonal elements in the SOC matrix are replaced by the corresponding MRCISD+Q energies calculated above. The calculated spectroscopic properties of the ground and low-lying electronic states are generally in good agreement with our experimental determinations. This work represents the first experimental investigation of the electronic and molecular structure of the WS molecule.