THE INFLUENCE OF NUCLEAR VOLUME AND ELECTRONIC STRUCTURE ON THE ROTATIONAL ENERGY OF PLATINUM MONOXIDE, PtO.

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The pure rotational spectra of seven isotopic species of platinum monoxide in its $X0^+$ electronic ground state have been measured with a cavity pulsed jet Fourier-transform microwave spectrometer. The molecules were prepared by laser ablation of Pt foil in the presence of O_2 and stabilized in a supersonic jet of argon. A multi-isotopomer Dunham-type analysis of the spectra produced values for Y_{01} and Y_{11}, along with unusually large values for the Born-Oppenheimer breakdown (BOB) parameters for both Pt and O. The values of the BOB parameters have been rationalized in terms of the molecular electronic structure and finite nuclear size (field shift) effects. A large negative ^{195}Pt effective nuclear spin-rotation constant has been rationalized in terms of the electron-nucleus dipole-dipole hyperfine constant. Precise internuclear separations have been evaluated.