THE OPEN-SHELL Xe-O_2 VAN DER WAALS COMPLEX: MICROWAVE SPECTRA AND $AB\ INITIO$ POTENTIAL ENERGY SURFACE

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An $ab\ initio$ potential energy surface of the open shell Xe-O_2 complex was calculated at the RCCSD(T) level of theory. The global minimum was found at a T-shape structure with a well depth of 137.0 cm^{-1}. Five rotational transitions of Xe-O_2 were measured using a pulsed-nozzle Fourier transform microwave spectrometer and assigned to the $^3\Sigma^-$ electronic ground state of the complex. Each transition shows magnetic hyperfine structure arising from interactions of the electronic magnetic moment with the earth′s magnetic field and these structures were reduced by the use of helmholtz coils. Hyperfine structures due to Fermi contact coupling between the electron spin of O_2 (S = l) and the ^{129}Xe (^{131}Xe) nuclear spin [I = 1/2 (3/2)] were also detected. The observed spectra were used to extract information about the geometric and electronic structure of the complex. The results provide detailed insight into the intermolecular interaction between Xe and paramagnetic oxygen. This may help to understand the relaxation mechanism of hyperpolarized ^{129}Xe in human blood in $in\ vivo$ magnetic resonance imaging experiments.