SPIN ORBIT CONFIGURATION INTERACTION CALCULATION OF THE ELECTRONIC STRUCTURE OF CUO

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Relativistic spin-orbit configuration interaction (SOCI) calculations have been performed to study the ground and excited electronic states of the linear CUO molecule. Six sets of geometries optimized by SOCI (COLUMBUS), density functional theory (ADF)[a], and CASPT2[b] methods have been investigated. The COLUMBUS geometries were optimized using the SOCI method and cc-pVTZ basis sets. With cc-pVDZ basis sets, SOCI calculations at the ADF and CASPT2 geometries give the $^1\Sigma_0^+$ as the ground state, the $^3\Phi_2$ being 19.08 and 17.41 kJ/mol higher respectively. With the larger cc-pVTZ basis sets, SOCI calculations at the ADF and CASPT2 geometries give the $^3\Phi_2$ as 3.43 and 5.52 kJ/mol lower than $^1\Sigma_0^+$ respectively. At the optimized COLUMBUS singlet geometry, the $^1\Sigma_0^+$ state is 49.41 kJ/mol lower than the $^3\Phi_2$ state. At the optimized COLUMBUS triplet geometry, the $^3\Phi_2$ state is 23.56 kJ/mol lower than the $^1\Sigma_0^+$ state. On the global surfaces, SOCI calculations predict the lowest $^1\Sigma_0^+$ energy to be 16.32 kJ/mol lower than the lowest $^3\Phi_2$ state. Our results are consistent with that of DC-CCSD(T) method,[c] but all comparisons are very dependent on the geometry.

[a] J. Li, B. E. Bursten, B. Y. Liang and L. Andrews *Science* **295**(2242), 2002.
[b] B. O. Roos, P. O. Widmark and L. Gagliardi *Faraday Discuss.* **124**(57), 2003.
[c] I. Infante and L. Visscher *J. Chem. Phys.* **121**(5783), 2004.