SPECTROSCOPIC CONSTANTS OF Co-CONTAINING RADICALS PREDICTED BY HIGHLY ACCURATE *AB INITIO* QUANTUM CHEMICAL CALCULATIONS

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We have been investigating the method to predict spectroscopic constants of metal-containing radicals, such as MgNC, MgCN, FeNC, FeCN, FeC, FeN, and CoCO, *etc.*, accurately enough for molecular spectroscopy by highly-correlated *ab initio* quantum chemical calculations. In this paper, we focus on the Co containing radicals, CoH and CoCN.

The simplest Co containing molecule, CoH, has already been studied extensively.[a] However, not only experimentally but also theoretically obtained spectroscopic constants of CoH vary widely, and hence the spectroscopic constants of CoH have not conclusively been determined yet. After examining many methods carefully, we found that the size-consistent method and the separation of nearly-degenerate excited states are necessary to describe the electronic states of CoH. In addition, we found that the present available basis sets are not sufficient to describe such specific electronic states of CoH accurately.

For CoCN, again a too short CN bond length, r_0(CN) = 1.1313(10) Å, has been determined for the $\tilde{X}\,^3\Phi_{\Omega=4}$.[b] Our predicted r_e(CN) for the $\tilde{X}\,^3\Phi_i$ at the MR-SDCI+Q+Relativistic-correction level is 1.171 Å, which falls in the normal range of distance established for many CN-containing molecules.

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[a] See for example: S.P. Beaton, K.M. Evenson, T. Nelis, and J.M. Brown, *J. Chem. Phys.*, **89**, 4446-4448 (1988); R. S. Ram, P. F. Bernath, and S. P. Davis, *J. Mol. Spectrosc.*, **173**, 158-176 (1995); D.P. Chong, S.R. Langhoff, C.W. Bauschlicher, Jr., S.P. Walch, and H. Partridge, *J. Chem. Phys.*, **85**, 2850-2860 (1986); M. Freindorf, C. M. Marian, and B. A. Hess, *J. Chem. Phys.*, **99**, 1215-1223 (1993).

[b] P. M. Sheridan, M. A. Flory, and L. M. Ziurys, *J. Chem. Phys.*, **121**, 8360-8368 (2004).