1P19

Strange Behavior of DK Relativistic Correction on the CoH ab initio Calculation

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For CoH, we previously performed the non-relativistic full-valence ab initio MR-SDCI+Q and MRCPF level calculations using Slater type basis functions.[1] Molecular structure and molecular constants obtained were in good agreement with observations though the relativistic correction is indispensable for the highly accurate ab initio calculation of the transition metal complex. In order to confirm the effect of relativistic correction for CoH, we carried out ab initio calculations with the third order Douglus-Kroll (DK3) relativistic correction using Gaussian type basis functions. C_{2v} symmetry was assumed and MOLPRO2010.1 was applied for all calculations. Results are shown in Table 1.

The bond lengths (r_e and r_0) and vibrational frequencies (ω_e and ν) obtained by the relativistic full-valence ab initio MR-SDCI+Q calculations: 1), 2) and 3), are short and high in comparison with observations, respectively. Namely, in the full-valence level, the DK3 correction is overshooting for relativistic effect whereas the non-relativistic result: 4) is in the best agreement with observation. The inclusion of the inner shell (3s and 3p) effects of Co atom drastically improves the DK3 result: 5) but worsens the non-relativistic result: 6).

Table 1. Equilibrium structure and vibration Frequency of $^3\Phi$ CoH at various level of calculations

		Active space		DK or				
	Basis sets[a)]	CASSCF	MR-SDCI+Q	NR	r_e /Å	r_0 /Å	ω_e /cm^{-1}	ν /cm^{-1}
0)	Exp. (*cf.*, Tomonari et al (2007)[1)])				1.516	1.526	1925	1856
1)	5ZP ANO-RCC	3d,4s,4p	3d,4s,4p	DK3	1.507	1.523	2002	1965
2)	aV5Z-DK	3d,4s,4p	3d,4s,4p	DK3	1.507	1.523	2004	1973
3)	Sap-aQZP-DK	3d,4s,4p	3d,4s,4p	DK3	1.506	1.533	2010	1987
4)	Sap-aQZP-NR	3d,4s,4p	3d,4s,4p	NR	1.517	1.531	1923	1879
5)	Sap-aQZP-DK	3s,3p,3d,4s,4p	3d,4s,4p	DK3	1.516	1.522	1919	1845
6)	Sap-aQZP-NR	3s,3p,3d,4s,4p	3d,4s,4p	NR	1.509	1.519	1970	1843

a) Sap: Sapporo GTF[2]

[1] M. Tomonari, R. Okuda, U. Nagashima, K. Tanaka, T. Hirano, J. Chem. Phys., 126, 144307 (2007).
[2] http://setani.sci.hokudai.ac.jp/sapporo/Welcome.do