COMPUTATIONAL MOLECULAR SPECTROSCOPY: THE EQUILIBRIUM BOND LENGTH OF $\tilde{X}\,^3\Phi$ CoH

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Two distinctly different values of r_e(Co-H) have been reported for the CoH molecule: One is 1.5138435(80)[a] Å from the Beaton and Brown group (BB), determined by far-infrared laser magnetic resonance spectroscopy, and the other is 1.531291(8)[b] Å or 1.532664(16)[c] Å from the Ram and Bernath group (RB) determined by near-infrared emission spectroscopy. The BB group analyzed spectra at the Hund's case (a) limit and the RB group at the Hund's case (c). The rotational constants determined by the two groups are similar in magnitude: $B_{\Omega=4}$ and $B_{\Omega=3}$ by BB are 7.13680(16) and 7.27450(13) cm^{-1}, respectively, and $B_{\Omega=4}$ and $B_{\Omega=3}$ by RB in 2006 are 7.136591(160) and 7.27614(21) cm^{-1}, respectively. The difference in r_e(Co-H) is caused by the fact that the BB group apply the spin-orbit correction $B_\Omega = B_0 + 2{B_0}^2\,\Sigma/(A_{SO}\Lambda)$ to the rotational constant, whereas the RB group do not. It should be noted that although the $^3\Phi_{\Omega=3}$ state is perturbed, we can derive almost the same r_e(Co-H) values of 1.5179 Å and 1.5180 Å from the $B_{\Omega=3}$ values reported from BB and RB groups, respectively. Here, spin-orbit correction is not needed since $\Sigma = 0$. Our best *ab initio* value of r_e is 1.507 Å (*J. Chem. Phys.*, in press) and 1.509 Å (unpublished) at the level of MRCPA(4)/STO using the ALCHEMY II program. Since BB used the spin-orbit coupling constant $A_{SO} = -221.5$ cm^{-1} determined from the experimentally observed spin-splitting, the unperturbed A_{SO} becomes larger than theirs, and hence the r_e value reported by BB group based on $B_{\Omega=4}$ should be a little shorter than 1.5138 Å, which coincides with our *ab initio* predicted value.

[a] S. P. Beaton, K. M. Evenson, and J. M. Brown, *J. Mol. Spectroscopy*, **164**, 395-415 (1994).
[b] R. S. Ram, P. F. Bernath, and S. P. Davis, *J. Mol. Spectroscopy*, **175**, 1-6 (1996).
[c] I.E. Gordon, R.L. LeRoy, and P.F. Bernath, *J. Mol. Spectroscopy*, **237**, 11-18 (2006).