Dissociation of the fluorine molecule: A benchmark study

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A small but notable discrepancy exists between the two most recently published [1, 2] dissociation energies for the fluorine molecule and, consequently, heats of formation for the F atom. The difference between the two atomic heats of formation in question is 0.20 kJ/mol, which is considerably larger than the sum, 0.11 kJ/mol, of the error bars associated with the corresponding results. In addition, in a theoretical study [3] the existence of a small and uncertain barrier along the dissociation curve of the molecule with a height of approximately $+40$ $\mu\mathrm{E}_h$ ($\sim$0.10 kJ/mol) has been reported near the internuclear separation of 4 Å, while in another computational investigation [4] no such barrier has been found. In the case of its negligence during the evaluation of the raw experimental data, the barrier may introduce and additional error to the results which may be at least as high as the barrier height itself.

In order to resolve the discrepancies between the dissociation energy [$D_0(\mathrm{F}_2)$] and atomic heat of formation [$\Delta_f H_0^\circ(F)$] values, a highly accurate coupled-cluster based composite theoretical model chemistry has been utilized. The protocol involves contributions of up to pentuple excitations in coupled-cluster theory amplifying with additional corrections beyond the non-relativistic and Born–Oppenheimer approximations. The augmented core-valence counterparts of the correlation consistent basis set families, aug-cc-pCV*X*Z, have been used up to octuple-ζ quality. Our best theoretical estimates for $D_0(\mathrm{F}_2)$ and $\Delta_f H_0^\circ(\mathrm{F})$ obtained in this study are 154.95 ± 0.48 and 77.48 ± 0.24 kJ/mol, respectively. The relatively high error bars are mostly due to the considerably large contributions from the relativistic effects carrying large uncertainties.

In order to prove or disprove the existence of the small barrier on the dissociation curve of F_2, extensive multi-reference configuration interaction and coupled-cluster calculations based on all-electron CASSCF reference orbitals have been performed. The extrapolated results from aug-cc-pCV*X*Z (*X*=T,Q,5) calculations clearly indicate that the barrier indeed exists. It is located at 3.80 ± 0.20 Å along the dissociation curve with a height of 42 ± 10 $\mu\mathrm{E}_h$ ($\sim$0.11$\pm$0.03 kJ/mol).

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[3] L. Bytautas and K. Ruedenberg, *J. Chem. Phys.*, 130, 204101, 2009.

[4] F. A. Evangelista, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.*, 127, 024102, 2007.