

Supporting Information

Pd_nCO (*n* = 1,2): Accurate *Ab Initio* Bond Energies, Geometries, and Dipole Moments and the Applicability of Density Functional Theory for Fuel Cell Modeling

Nathan E. Schultz, Benjamin Gherman, Christopher J. Cramer, and Donald G. Truhlar

Department of Chemistry and Supercomputing Institute, University of Minnesota, 207 Pleasant Street Southeast, Minneapolis, MN 55455, USA

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In addition to the CCSD(T) calculations for Pd₂ we have examined $D_e(\text{Pd}_2)$ with complete activation space second-order perturbation theory¹ (CASPT2) and the MQZ basis set with correlation an active space of 20 orbitals and 36 electrons. This corresponds to correlation of the $4s^24p^6$ electrons on Pd; as such the calculations are denoted “sc” for small core (see Section 3.D of printed article).

The results are given in Table S-1. The CASPT2/MQZ-sc calculation predicts $D(\text{Pd}_2) = 25.2$ kcal/mol and the recommended^{2,3} experimental value is 24 kcal/mol. The agreement between CASPT2/MQZ and experiment is ~ 1 kcal/mol. However, we believe that this agreement is fortuitous, as the experimental number is unreliable. The experimental number was determined by third-law analysis where a critical part the analysis is the evaluation of the molecular partition function. The molecular parameters used in the evaluation of the partition function in this case were taken from theoretical calculations.⁴ The calculations by Shim *et al.*⁴ are non-relativistic and very inaccurate. For example, the calculations by Shim *et al.*⁴ predict the incorrect ground state and have significant errors in their calculated excitation energies. The effect of this incorrect computational data on the experimental value is potentially non-negligible, and correcting the “experimental” value is expected to worsen the agreement between the CASPT2 calculations and experiment.

The excitation energies for the Pd atom, T_e , are given in Table S-1. The CASPT2/MQZ-sc calculations overestimate the experimental value by 2 kcal/mol, whereas the CCSD(T)/MQZ-sc calculations underestimate the value by 1 kcal/mol. The printed article states that methods that do poorly for the T_e of the atom also do poorly for $D_e(\text{Pd}_2)$.

An additional reason to doubt the CASPT2 calculation is its predicted $r_e(\text{Pd}_2)$ of 2.330 Å, which is 0.09 Å shorter than the CCSD(T)/MQZ-sc bond length of 2.417 Å. The CASPT2 bond length is considered incorrect as not a single DFT method presented in the text predicts a bond length shorter than 2.46 Å, so it is unlikely that the correct $r_e(\text{Pd}_2)$ is near 2.3 Å. It is surprising that not a single DFT method predicts an $r_e(\text{Pd}_2)$ shorter than 2.417, but $r_e(\text{Pd}_2) = 2.417$ Å appears more reasonable when compared to DFT than does $r_e(\text{Pd}_2) = 2.330$ Å.

The analysis of static correlation was presented in the text, and we noted that Pd₂ has mild multi-reference character and can most likely be treated using single-reference methods such as CCSD(T). In situations such as this, we have more confidence in the CCSD(T) method, which has a poor reference function relative to CASPT2, but has a more accurate treatment of the electron correlation. We have noted a few discrepancies between CCSD(T)/MQZ-sc and CASPT2/MQZ-sc in this section, but our analysis suggests that the difference is not due to multi-reference character but more likely is due to the treatment of electron correlation.

Table S-1. Properties for Pd₂ calculated with the MQZ basis set

	CASPT2	CCSD(T)	experiment
T_e	21.1	17.8	18.8
$D_e(\text{Pd}_2)$	25.2	17.5	24 ± 4
$r_e(\text{Pd}_2)$	2.330	2.417	

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- (4) Shim, I.; Gingerich, K. A. *J. Chem. Phys.* **1984**, *80*, 5107.