

0.06 cm⁻¹ DISCREPANCY FOR Li₂ → 2Li AND 0.994 cm⁻¹ FOR C → C⁺ BETWEEN LABORATORY AND COMPUTER SPECTROMETERS.

NIKESH S. DATTANI^a, *Department of Chemistry, Kyoto University, Kyoto, Japan.*

The energy at the empirical bond length of Li₂(1³Σ_u⁺) of 4.1700 Å^b was obtained at all-electron FCI level with an aug-cc-pCV5Z-NR basis set, all-electron CCSDT(Q) with aug-cc-pCV7Z-NR, and all-electron CCSD(T) with aug-cc-pCV8Z-NR; along with corrections due to special relativity converged with respect to electron correlation and basis set size using the spin-free Dirac-Coulomb Hamiltonian, and further such corrections at the Hartree-Fock level using the Breit and Gaunt Hamiltonians. Corrections to the point-size nucleus approximation were calculated but found to be negligible. The result was compared to the lowest energy of the best empirical potentials^b with the empirical Born-Oppenheimer breakdown corrections removed, making it essentially an infinite-mass to infinite-mass comparison. The discrepancy between the energy obtained from laboratory spectroscopy and the energy obtained completely by the computer was only 0.06 cm⁻¹, which is of the same order of magnitude as the uncertainty on the empirical value, which is ±0.007 cm⁻¹ before including the added uncertainty coming from the Born-Oppenheimer breakdown parameter u_0 which itself has an uncertainty of 0.01 cm⁻¹. It is discussed what is necessary for the computer spectrometer to outperform the laboratory spectrometer.

The ionization energy of the carbon atom was calculated at all-electron FCI level with aug-cc-pCV8Z-NR and aug-cc-pCV7Z-NR basis sets (the latter only for basis set extrapolation); along with corrections due to special relativity converged with respect to electron correlation and basis set size using the 1 e^- X2C Hamiltonian, further corrections using state-averaged Dirac-Fock for the contribution from the Breit Hamiltonian and some QED contributions; along with DBOC corrections to the clamped nucleus approximation converged with respect to electron correlation and basis set size. Again, corrections to the point-size nucleus approximation were calculated but found to be negligible. The final energy was compared to the very recent experimental value published by NIST^c with the experimental spin-orbit lowering of 12.672508 cm⁻¹ removed. The discrepancy was 0.994 cm⁻¹ compared to the ±0.009 cm⁻¹ uncertainty in the laboratory value.

^anik.dattani@gmail.com

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^cHaris K., Krimada A. E., (2017) arXiv:1704.07474.