HeH^+, HeD^+, HeT^+, BeH, BeD, and BeT POTENTIALS THAT REPRODUCE ALL MEASURED ENERGY TRANSITIONS, AND FOR THE HeH^+ ISOTOPOLOGUES ARE ACCURATE UP TO THE INCLUSION OF RELATIVISTIC AND LEADING FOURTH ORDER QED EFFECTS IN THE LONG-RANGE REGION BEYOND AVAILABLE EXPERIMENTS

STASZEK WELSH, *Physical and Theoretical Chemistry Laboratory, Oxford University, Oxford, United Kingdom*; MARIUSZ PUCHALSKI, *Department of Chemistry, Adam Mickiewicz University, Poznan, Poland*; GRZEGORZ LACH, *, International Institute of Molecular and Cell Biology, Warsaw, Poland*; TUNG WEI-CHENG, *Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA*; LUDWIK ADAMOWICZ, *Department of Chemistry and Astronomy, University of Arizona, Tuscon, AZ, USA*; NIKESH S. DATTANI (dattani.nike@gmail.com) , *Department of Chemistry, Oxford University, Oxford, United Kingdom*.

According to the big bang theory, HeH^+ was the first molecule ever produced in our universe, along with He_2^+. It is also the simplest two-electron molecular system and lightest heteronuclear molecule, with a stable ground electronic state, aside from the isotopologues of H_2. These facts make HeH^+ very interesting for experimental studies of the early universe and theoretical studies of isotope effects including Born-Oppenheimer breakdown (BOB), as well as an extremely important benchmark system for *ab initio* methods. However, no spectroscopic measurements, nor *ab initio* calculations have been reported for HeT^+, and the most accurate empirical potentials for HeH^+ and HeD^+ are 15 years old and are unreliable outside of the data range. We build the most accurate analytical empirical potentials and BOB functions for HeH^+ and HeD^+ to date. These BOB functions are then used to predict the HeT^+ potential, and are in excellent agreement with our *ab initio* potential for HeT^+. Outside the data-range, the MLR (Morse/long-range) model forces the analytic empirical potential to become the theoretically correct long-range potential based on the multipole polarizabilties of He. We include the dipole and quadrupole polarizabilities. The quadrupole value includes finite-mass and relativistic corrections, and an estimate of the leading α^3 QED corrections. The dipole value includes finite-mass, relativistic, and QED corrections up to the leading term of the α^4 effects.

Being the simplest neutral open shell molecule, BeH is also a very important benchmark system for *ab initio* calculations. However, the most accurate empirical potentials and BOB functions for this system are nearly a decade old and are not reliable in the long-range region. Particularly, the uncertainties in their dissociation energies were about ± 200 cm^{-1}, and even the number of vibrational levels predicted was at the time very questionable, meaning that no good benchmark exists for *ab initio* calculations on neutral open shell molecules. We build new empirical potentials for BeH, BeD, and BeT that are much more reliable in the long-range. Being the second lightest heteronuclear molecule with a stable ground electronic state, BeH is also very important for the study of isotope effects, such as BOB. We extensively study isotope effects in this system, and we show that the empirical BOB functions fitted from the data of any two isotopologues, is sufficient to predict crucial properties of the third isotopologue.