

Very accurate rovibrational transitions of HeH^+ in the ground electronic state

Keith Jones^a, Monika Stanke, Ludwik Adamowicz^{a,b}

^a*Department of Chemistry and Biochemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.*

^b*Department of Physics, University of Arizona, Tucson, Arizona 85721, U.S.A.*

HeH^+ rovibrational transitions are calculated using a very accurate Born-Oppenheimer potential energy surface, which is supplemented with adiabatic and non-adiabatic corrections for nuclear motion, and relativistic corrections for electron motion. Comparisons are made with leading experimental data.

I. INTRODUCTION

HeH^+ is the lightest, bound heteronuclear diatomic molecule. It is composed of the two most abundant elements in the universe. The presence of HeH^+ in interstellar space and planetary nebulae is expected [1–3], and steady state abundances of the molecule under different conditions have been calculated [4] although it has yet to be observed [5, 6].

The existence of HeH^+ was confirmed in 1925 by mass spectrometry of discharges containing He and H [7]. Optical measurements would follow decades later. HeH^+ has a permanent dipole moment, and very accurate transition energies can be measured because of this. In 1979, the first rovibrational transitions for HeH^+ ever measured, 5 transitions in total, were in the fundamental band and the first hot band of the electronic ground state [8] with uncertainties of 0.002 cm^{-1} . In the following decades, many more pure rotational [9–11] and rovibrational [11–16] transitions were measured, for multiple isotopologues [9, 12, 16], with many of the later measurements collected using tunable diode lasers [10, 15, 16]. There were also transitions between bound and quasibound levels measured [13].

It is important for computational models to keep up with the accuracy of experimental measurements in order for the unobserved transitions in this system calculated with those models to be assumed correct. The most common way to model diatomics is to construct a potential energy surface, for the internuclear coordinate, and then solving the radial Schrödinger equation to acquire the rovibrational levels.

The first potential energy surface for HeH^+ that was done accurately used a 64-term generalized James-Coolidge expansion for the wavefunction [17], which allowed the approximation of the equilibrium bond length and the dissociation energy. Later, a potential energy surface of HeH^+ between 0.9 and 9 au was constructed using an 83-term variational wave function expansion in elliptic coordinates with linear and non-linear variational parameters [18, 19], which was later improved by using a larger basis set and adiabatic corrections [20]. A potential energy curve for HeH^+ was fitted using experimental transitions and 19 tunable parameters [21]. Recently, a very accurate Born-Oppenheimer (BO) potential energy surface was constructed for HeH^+ in a basis of "asymptotically correct generalized Heitler-London

functions” [22], followed by adiabatic, non-adiabatic, relativistic, and radiative corrections, which allowed the accurate calculation of the rovibrational transitions [6].

Explicitly correlated Gaussian functions (ECGs) have been used to describe HeH^+ with accurate single point calculations carried out for different electronic states [23] at the equilibrium distance and a potential energy surface developed in 2012 which incorporated adiabatic and non-adiabatic corrections [24].

ECGs have also been used to describe HeH^+ without assuming the Born-Oppenheimer approximation. All rotationless vibrational states in the ground electronic have been calculated [25] with relativistic and radiative corrections [26, 27]. This has also been done with complex basis functions [28]. These wavefunctions are probabilistic functions of both electrons and nuclei and can be used to glean insight into molecular structure that is not possible from the BO description.

II. METHODOLOGY

Methodology

III. RESULTS

Results

IV. CONCLUSIONS

Conclusions

V. ACKNOWLEDGEMENTS

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