Accurate *ab initio* potential energy curve of $\mathbf{X}^2\Pi$ state and high-temperature $\mathbf{A}^2\Delta$ - $\mathbf{X}^2\Pi$ fluorescence spectra for CH radical

Jing Guo, Bing Yan*, and De-Ling Zeng

Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China

Abstract. In present study an accurate *ab initio* potential energy curve of CH($X^2\Pi$) has been determined at the complete basis set limit. The core-valence corrections and relativistic corrections including scalar relativity and spin-orbit coupling are determined. The vibrational and rotational levels are calculated based on fitted potential energy curve. Total 19 vibrational levels are found for ^{13}CH ground state, and comparing with available experimental data, the deviation is less than 15 cm^{-1}. The dissociation energy is calculated within 50 cm^{-1} of the experimental value 29358 cm^{-1}. The $A^2\Delta$ - $X^2\Pi$ electric transition dipole moment function is calculated, and the high-temperature fluorescence spectra arising from $A^2\Delta$ - $X^2\Pi$ transition are simulated.

1 Introduction

Early in 1919 the CH radical was firstly detected by spectra analysis [1], and it becomes the subject of numerous theoretical and experimental investigations[2 4] since that time for its widely presence in the sun, stellar atmospheres, comets, interstellar spaces, flames and explosions. As most-studied free radical, previous spectroscopic data of CH have been collected and compiled by Huber and Herzberg[5] and are available online in NIST databases[6]. The spectroscopic studies on CH radical in optical, infrared, far-infrared, and microwave regions have well characterized ground and some excited states below

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*Corresponding author. *Email address:* `yanbing@jlu.edu.cn` (B. Yan)

8eV[4,6,8]. While for some perturbed states via predissociation or those with weak transitions intensity, the *ab initio* studies are need to explore the molecular spectroscopic constants of high vibrational levels and molecular properties, such as equilibrium geometry, dissociation energy, dipole moment *et al.* For $X^2\Pi$ state of CH and its isotopic systems, only low vibrational levels spectroscopic constants are available because of the limitations in measurements. The high vibrational and rotational levels of $A^2\Delta$ state, crossing with $B^2\Sigma^-$ state, are difficult to characterize via A-X transition spectral experiments.

The *ab initio* investigations for CH became lasting interests for theoretical workers since 1954 [9]. In the past several decades, the spectroscopic constants of $X^2\Pi$ state were calculated using different theoretical approach including Hatree-Fock(HF), couple cluster, and configuration interaction(CI) methods with different number of basis functions [10,11]. Previous *ab initio* results [2] for equilibrium bond distance r_e of CH($X^2\Pi$) ranges from 1.09Å to 1.204Å, the smallest deviation between theoretical value and 1.1196Å of experimental value [6] is less than 10^{-3}Å. The error for harmonic frequency ω_e is at least 10 cm^{-1}, and that for anharmonic error $\omega_e x_e$ is in the range of 2 20 cm^{-1} in previous *ab initio* investigations[2] except those in Dunning's benchmark calculation [11]. While few early theoretical studies considered the relativistic effects, core electrons correlation corrections, and the complete basis set(CBS) limit extrapolation for the potential energy curve(PEC). And to the best of our knowledge, no *ab initio* reports for the spectroscopic constants of total vibrational and rotational levels with high level of theory as current electronic structure theory can yield.

In present work, the PECs of $X^2\Pi$ state were calculated with valence-splitting basis sets and extrapolated to CBS limit. The scalar relativistic effect, that is the mass-velocity and Darwin terms, the spin-orbit coupling (SOC) splitting, and the core correction energies were then evaluated. The total vibrational and rotational spectrum of $X^2\Pi$ state were obtained and compared with available experiments. The $A^2\Delta$- $X^2\Pi$ transition dipole moment functions were calculated for simulation of vibrational-resolved high-temperature $A^2\Delta$- $X^2\Pi$ fluorescence spectra which are important to explore the dynamics processes in combustion and plasma.

2   Methods and computational details

The C_{2v} symmetry was used in calculations, and the molecular axis was located along z-axis, thus the $^2\Pi$ and $^2\Delta$ states are represented by $^2B_1+^2B_2$ and $^2A_1+^2A_2$, respectively. The zeroth-order reference energies were calculated using full valecne complete active space self consistent field (CASSCF)[12] wavefunctions with all-electron correlation-consi stent polarized valence X-zeta, aug-cc-pVXZ(X=Q(4),5,6), basis sets [11]. The valence electrons correlation energies were evaluated using internal contraction multireference CI(ic-MRCI) with singly and doubly excitations scheme as implemented in the Molpro[12] package. The Davidson corrections followed MRCI calculations (MRCI+Q) were used for size consistency consideration. For the X-tuple zeta basis sets, the zeroth-order