

Rotation-vibration spectra for ground state of NaH and its isotopes with explicitly multireference configuration interaction method

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Abstract. High-level *ab initio* calculations utilizing explicitly correlated multi-reference configuration interaction method (MRCI-F12), considering Davidson modification(Q), core-valence correlation correction(CV) and scalar relativistic correction(SR), were performed to compute the Born-Oppenheimer potential energy curve (PEC) of the ground state $X^1\Sigma^+$ of NaH. On the base of the PEC, we obtained vibrational and rotational energy levels information of the ground state $X^1\Sigma^+$. The vibrational and rotational spectroscopic constants of $X^1\Sigma^+$ were compared with the available experimental values. We also report rotation-vibration spectra of the ground state for the isotopes of NaH, NaD and NaT molecules. The equilibrium internuclear distances R_e and dissociation energies D_e were calculated to be 1.8865Å and 15823.29cm⁻¹ for the ground state $X^1\Sigma^+$ of NaH, which are in good agreement with the experimental results of 1.8859Å and 15815±5cm⁻¹.

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Key words: MRCI-F12, NaH, rotational-vibration constants

1 Introduction

Due to its important role in regulating the fractional ionization in molecular clouds, astrophysicists are interested in sodium chemistry which strongly influences ion-molecule dynamics in the interstellar space [1]. Astronomers suppose interstellar sodium is in the form of gas-phase NaH [2, 3]. And it is important to know the abundance information of sodium hydride in the interstellar medium for a better understanding of interstellar sodium chemistry. The investigations on the rotation-vibration spectrum for the ground state $X^1\Sigma^+$ of NaH are motivated by its astrophysical significance.

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Since the early 1930s, several experimental [4-15] and theoretical computational [16-27] studies on the spectra and interactions of NaH have been reported. In the aspect of the experiment, NaH was the first studied in 1930 by Hori, who observed and analyzed $X^1\Sigma^+-A^1\Sigma^+$ bands in absorption [4]. Next year, Hori reported the emission spectrum of $X^1\Sigma^+-A^1\Sigma^+$ bands for NaH [5]. In 1934, Olsson [6] reported the new NaH measurements together with the NaD data of absorption spectroscopy in the spectral region of $358 \text{ nm} \leq \lambda \leq 445 \text{ nm}$ cover vibrational levels in the range $0 \leq v'' \leq 3$ and $1 \leq v'' \leq 20$. In 1948, Panhhurst observed on the spectrum of NaH and extended it to longer wavelengths (from 4600 \AA to 6450 \AA) [7]. After 30 years, in 1988 Magg and Jones used a tunable diode laser spectrometer to measure the first infrared vibrational for NaH [9]. One year later, Maki and Olson measured the infrared spectrum of NaH using a Fourier transform spectrometer [10]. In 1993, Rafi *et al.* [11] reported new band origins and $A^1\Sigma^+$ state B_v and D_v rotational constants of $v''(X^1\Sigma^+) = 0$ bands for $v'(A^1\Sigma^+) = 13-22$ and of $v''(X^1\Sigma^+)=1$ bands for $v'(A^1\Sigma^+)=12-25$. In 1996, Lochbrunner *et al.* [12] reported NaH band absorption from $v''(X^1\Sigma^+) = 0-3$ into $v'(A^1\Sigma^+) = 2-15$ and NaD bands from $v''(X^1\Sigma^+) = 0-2$ into $v'(A^1\Sigma^+) = 5-17$. In 2000, Pesl *et al.* [13] measured high-resolution spectroscopy data for the $A^1\Sigma^+-X^1\Sigma^+$ transition. Most recently, Huang *et al.* [14, 15] observed vibrational quantum numbers of up to $v''=21$ in the ground state of NaH.

Theoretically, first computational work was reported in 1975, Sachs and Hinze used multiconfigurational method to calculate first six states of NaH [16], Sachs and Hinze published the transition moments, band strengths and line strengths for NaH [18] and reported the rotation-vibrational analysis for three low-lying states of NaH and NaD [17]. Since then, lots of computational works [19-24] were engaged in the electronic states information of NaH. In 2004, Brian and Philip R [25] used basis set extrapolation technique in combination with highly correlated *ab initio* calculations obtained nearly exact properties for the $X^1\Sigma^+$ electronic ground state of the NaH and NaD molecule, and found 20 vibrational levels for NaH. In 2004, Yang *et al.* [26] utilized MRCI method with Davidson correction calculated PECs and obtained spectroscopic parameters of first few electronic states of NaH. More recently, Sadru-Dean *et al.* [27] summarized previous experimental and theoretical reports, analyzed the dissociation energies and potential energy functions for the ground $X^1\Sigma^+$ and "avoided-crossing" $A^1\Sigma^+$ states of NaH.

In this work, we performed the explicitly correlated multireference configuration interaction method for the lowest $X^1\Sigma^+$ state of the sodium hydride with Davidson correction (+Q), core-valence (CV) effect and scalar relativistic (SR) effect. Based on computed adiabatic PEC of the $X^1\Sigma^+$, the vibrational energy spacings $G_{v+1/2}$, vibrational energy terms G_v , the vibration-dependent rotational constant B_v , and centrifugal distortion constant D_v of ground state were also obtained by numerically solving the ro-vibrational Schrödinger equations. The vibrational and rotational constants of the $X^1\Sigma^+$ state for NaD and NaT are also presented in this work.