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Accurate potential energy function and spectroscopic properties of NS ($X^2\Pi$) via extrapolation to the complete basis set limit

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Abstract. Potential energy curves (PECs) for the ground electronic state of NS are acquired by means of fitting the *ab initio* energies computed at the multi-reference configuration interaction method with the Davidson correction in combination with a series of correlation-consistent basis sets from Dunning: aug-cc-pVXZ (X = T, Q, 5 and 6). In order to obtain PECs with high accuracy, the PECs computed with aug-cc-pV(Q,5)Z basis sets are extrapolated to the complete basis set limit. Such PECs are then used to fit the analytical potential energy functions (APEFs) with the extended Hartree–Fock approximate correlation energy method. Based on the APEFs of NS($X^2\Pi$), reliable and accurate spectroscopic parameters are obtained. By solving the radial Schrödinger equation numerically, we can acquire the complete set of vibrational levels, inertial rotation constant, centrifugal distortion constants and classical turning points when J = 0. As a whole, our research data can be regarded as a reference for prospective research on the NS molecule.

1. Introduction

The NS radical as a prototype molecule is studied extensively in laboratory spectroscopy and interstellar space. On the one hand, it is of fundamental importance in the interstellar fields of nitrogen chemistry [1] and sulfur chemistry [2]. For example, it was first identified in Sgr B2 [3], then was detected in cold dark [4,5] and in warm [6] interstellar clouds, and recently was observed in Comet Hale-Bopp [7]. On the other hand, the NS is also important in solid-state chemistry and in combustion chemistry because the $(NS)_x$ polymers have metallic conductivity properties [8].

The NS radical has been the topic of wide experimental and theoretical researches for ages. As early as 1932, the two bands of C–X system and A–X system from 2300 Å to 2700 Å in emission of the NS radical were found by Bakker and Fowler [9]. Zeeman [10] gauged the (0, 1) and (0, 0) γ bands, then determined the coupling constant A (223.03 cm^{-1}) at the ground electronic state ($X^2\Pi$) in 1951. Since 1966, there have been a number of experiments [11–25], in which the accuracy of the spectroscopic parameters have been improved. In 2007, Wang *et al.* [26] published the resonance-enhanced multiphoton ionization spectroscopy on the $B^2\Pi$ and $B'^2\Sigma^+$ of NS and acquired detailed spectroscopic parameters of both the excited state $B'^2\Sigma^+$ and the ground state $X^2\Pi$.

In theory, the early *ab initio* work on the NS radical was performed by O'Hare [27] in 1970, determining the ground state dissociation energy by the Hartree-Fock-Roothann *ab initio* calculations. Subsequently, Bialski and Grein [20] in 1976 made the first *ab initio* computations on several low-lying excited states of the NS using the configuration interaction (CI) and minimal basis sets of Slater-type orbitals. In 1985, Lie *et al.* [28] computed the low-lying valence and Rydberg states of NS employing CI approach. From then on, a number of *ab initio* calculations [8,28,29–38] have been done, in which a series of spectroscopic constants have been confirmed. Very recently, Gao *et al.* [39] studied the spectroscopic properties of the low-lying electronic states of the NS by using *ab initio* based MRCI+Q+DK method with all-electronic aug-cc-pV5Z basis set.

As a whole, the theoretical achievements have concluded a range of spectroscopic information, matching well with the effective experiment data. However, the selected spectroscopic properties from all the theoretical and experimental results basically focus attention on the spectroscopic constants (R_e, D_e, B_e, ω_e, $\omega_e\chi_e$ and α_e). There is a little available data in the other literature calculating its vibrational manifolds (vibrational levels, centrifugal distortion constants, inertial rotation constants and classical turning points with so helpful in the rovibrational transition computations. The accurate analytical potential energy functions (APEFs) of NS($X^2\Pi$), which is significant in the spectroscopic dynamics investigations and spectroscopic experiments. All these motivate us to structure highly precise APEFs and investigate more complete spectroscopic properties of NS($X^2\Pi$).

In the work, we calculate the PECs of the NS($X^2\Pi$) are studied with the high precision valence internally contracted multi-reference configuration interaction (MRCI(Q)) method [40,41] in combination with a series of correlation-consistent basis sets of Dunning and coworkers [42–44] in the valence range, namely aug-cc-pV(X+d)Z and aug-cc-pVXZ (X = T, Q, 5 and 6), which are hereinafter expressed as AVXdZ and AVXZ, respectively. In order to extrapolate the PECs computed at

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AV(Q,5)Z to the complete basis set (CBS) limit, we employed the uniform singlet- and triplet-pair extrapolation (USTE) protocol [45]. The PECs are fitted to the APEFs using the extended Hartree–Fock approximate correlation energy method (EHFACE) [46,47]. Based on the APEFs of NS($X^2\Pi$), reliable and accurate spectroscopic parameters are obtained. In theory, with the potential attained at the MRCI/aug-cc-pVXZ level, a set of vibrational levels, centrifugal distortion constants, inertial rotation constants and classical turning points are acquired by numerically calculating the radial Schrödinger equation of nuclear motion when the rotational quantum number *J* = 0. As a whole, our research offers more detailed and precise researches on the spectroscopic information of the NS($X^2\Pi$), as compared with the previous theoretical data.

The paper is arranged as follows: section 2 introduces the theoretical approaches, such as *ab initio* calculations, the application of extrapolation and calculated the APEF formalism. In section 3 the results are discussed in detail. Finally, the conclusion is presented in section 4.

2. Theoretical methods

2.1.*Ab initio* calculations

The MRCI(Q) approach is one of the best methods to obtain the precise potential energy surfaces (PESs). In this work, we adopted the full valence complete active space self-consistent field (CASSCF) method [48], the computed results are regarded as a reference wave function for the MRCI(Q) investigations. MOLPRO 2012 [49] is a kind of program package about the quantum chemistry, in combination with the correlation-consistent basis sets of Dunning *et al.* [44, 50] has been used in the present calculation. It is worth nothing that N atom using AVXZ (X=T, Q, 5 and 6) basis sets and S atom using AVXdZ (X=T, Q, 5 and 6) basis sets. During the present calculation, C_{2v} point group symmetry is used including A1, A2, B1 and B2 four irreducible representations. For NS($X^2\Pi$), a total of 11 electrons distributed in the 2s and 2p orbitals of N and the 3s and 3p orbitals of S in the active space.

For each basis set, the calculations of NS($X^2\Pi$) PECs are applied for the internuclear distance arranging from 2.0 a_0 to 20 a_0. In order to calculate the reliable PECs of NS, the interval set to be 0.01 a_0 next the equilibrium position, the results of spectroscopic constants are more reliable. By closing the core orbitals in the CASSCF and not associating them in the MRCI(Q) computation to ignore the core effects. An important reason for employing the frozen core approximation is due to that the raw *ab initio* energies computed with comparatively inexpensive cost (AV(Q,5)Z) are subsequently extrapolated to the CBS limit, expressed as CBS/AV(Q,5)Z. So the extrapolation came true by extrapolation to the CBS limit of the CASSCF energies and via extrapolation of the electron correlation energies to the CBS limit.

2.2. Extrapolation to the CBS limit

In order to carry out the extrapolation, electronic energy in the MRCI(Q) calculation is expressed by a sum of two terms [45,51]

$$E_X = E_X^{CAS} + E_X^{dc}, \tag{1}$$

where the superscript CAS represents the complete-active space and the superscript dc represents the dynamical correlation energies, in addition the subscript X signifies that the electronic energy has been calculated in the AVXdZ and AVXZ basis set, respectively. The X = Q, 5 are used during the present calculation, which is expressed as USTE(Q,5).

Adopting the two-point extrapolation program suggested by Martin [52] and Karton the CAS energies are extrapolated to the CBS limit and validated by Varandas [45] for extrapolation of the CASSCF energy.

$$E_X^{CAS} = E_\infty^{CAS} + \mathrm{B}/X^\alpha, \tag{2}$$

where E_X^{CAS} is the energy when $\mathrm{X} \to \infty$ and α=5.34 is an effective decay index.

The USTE protocol [45,53] has been triumphantly implemented to extrapolate the dynamical correlation energies in MRCI(Q) calculations, which is extrapolated by the formula

$$E_X^{dc} = E_\infty^{dc} + \frac{A_3}{(X+\alpha)^3} + \frac{A_5}{(X+\alpha)^5}, \tag{3}$$

with A_5 is written as the auxiliary relation

$$A_5 = A_5(0) + cA_3^{5/4}, \tag{4}$$

where α=-3/8, c=-1.17847713, and $A_5(0)$ = 0.0037685459 are “universal-like” parameters [45]. Equation (3) could be converted to (E_∞, A_3) two-parameter rule, which has access to the actual extrapolation process.

2.3. APEF of the NS ($X^2\Pi$)

The diatomic PEC of NS($X^2\Pi$) has been imitated employing the EHFACE approach [46,47] which is expressed as

$$\mathrm{V} = \mathrm{V_{EHF}(R)} + \mathrm{V_{dc}(R)}, \tag{5}$$

where V_{dc}(R) and V_{EHF}(R) are two-body terms of the dynamical correlation and the extended Hartree–Fock (EHF) types, respectively.

The extended Hartree-Fock energy term V_{EHF}(R) is denoted as

$$\mathrm{V_{EHF}(R)} = -\frac{\mathrm{D}}{\mathrm{R}}\left(1 + \textstyle\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{a_i r^i}\right) \exp(\gamma \mathrm{r}), \tag{6}$$

where γ=γ_0[1+$\gamma_1$tan*h*(γ_2*r*)], *r* = *R* − R_e as the displacement from the equilibrium diatomic geometry; by means of the a least-squares fit the *D*, a_i (i = 1,...n) and γ_i (i = 0,1,2) are adjustable parameters to be acquired.

The latter term is fitted by

$$\mathrm{V_{dc}(R)} = -\textstyle\sum_{\mathrm{n}=6,8,10} \mathrm{C_n} \chi_\mathrm{n}(\mathrm{R}) \mathrm{R}^{-\mathrm{n}}, \tag{7}$$

where

$$\chi_\mathrm{n}(\mathrm{R}) = 1 - \exp(-\mathrm{A_n R}/\rho - \mathrm{B_n R^2}/\rho^2)^\mathrm{n}, \tag{8}$$

is damping function of the dispersion coefficient. Furthermore, A_n and B_n are miscellaneous functions and written as