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Accurate potential energy function and spectroscopic properties of NS (X²Π) via extrapolation to the complete basis set limit

L. Guo[a,b], H.Y. Ma [a], W. Shi [a] , L. L. Zhang[c], Y. Z. Song[c], Q. Guo[a,b],* and Y. Q. Li[a,b],*

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(X²Π), 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 (X²Π) 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 B²Π and B'²Σ⁺ of NS and acquired detailed spectroscopic parameters of both the excited state B'²Σ⁺ and the ground state X²Π.

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(X²Π), 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(X²Π).

In the work, we calculate the PECs of the NS(X²Π) 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

a. *Department of Physics, Liaoning University, Shenyang 110036, China*
b. *Lvyuan Institute of Energy & Environmental Science and Technology, Liaoning University, Shenyang 110036, China*
c. *College of Physics and Electronics, Shandong Normal University, Jinan 250014, China*
yqli@lnu.edu.cn gq.ly@126.com

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.

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

where E_X^{CAS} is the energy when $X \to \infty$ 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

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

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

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

where $\gamma = \gamma_0[1+\gamma_1 \tanh(\gamma_2 r)]$, $r = R - R_e$ 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

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

where

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

is damping function of the dispersion coefficient. Furthermore, A_n and B_n are miscellaneous functions and written as
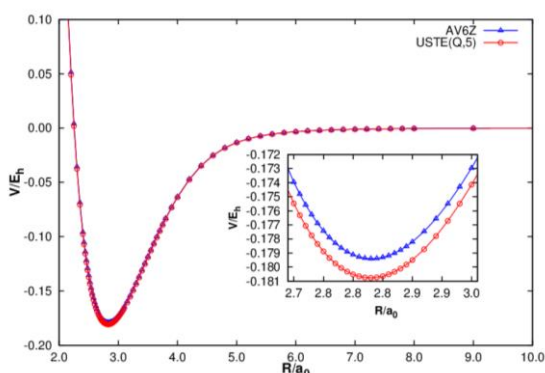
$$A_n = \alpha_0 n^{-\alpha_1}, \qquad (9)$$

$$B_n = b_0 \exp(-\beta_1 n), \qquad (10)$$

with α_0, β_0, α_1 and β_1 are general dimensionless parameters for all isotropic interactions: α_0 = 16.36606, β_0 = 17.19338, α_1=0.70172, β_1=0.09574. In addition, $\rho/a_0 = 5.5 + 1.25 R_0$, $R_0 = 2\left(\langle r_X^2 \rangle^{1/2} + \langle r_Y^2 \rangle^{1/2}\right)$ are the LeRoy parameter [54], and $\langle r_X^2 \rangle$ and $\langle r_Y^2 \rangle$ are the expectation values of squared radii for the outermost electron in atoms X and Y, respectively.

3. Results and discussion

3.1. The potential energy function

The diatomic PECs of the NS($X^2\Pi$) computed at the CBS limit [CBS/USTE(Q,5)] and the AV6Z level, acquired via the data computed employing the AV(Q,5)Z basis sets, is contrasted in Figure 1. The PECs at the AV6Z and the CBS/USTE(Q,5) calculations are smooth and converge. It can be seen from the Figure 1 that the CBS PEC gives slighter deeper well depth than the AV6Z PEC with the difference being ~ 0.0015 E_h. In this work, AV6Z is considered as a costly basis set, which always spends much more computing time than the AVQZ and AV5Z calculation. Employing the extrapolation of the CBS/USTE(Q,5) program [55,56], we will obtain the CBS PES using much less computing time.

Figure 1: Comparison of the PECs of NS($X^2\Pi$) calculated at AV6Z and extrapolated to the CBS limit using AV(Q,5)Z results.
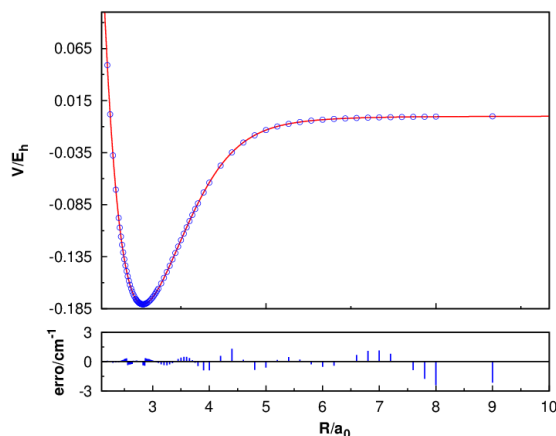
The EHFACE model [45-47] is then applied to conclude the APEFs for NS($X^2\Pi$) via least-squares fitting the PECs computed employing the AVXZ (X = T, Q, 5 and 6) basis sets. In addition, a more precise APEF is acquired by fitting the PEC computed at AV(Q,5)Z, which are then extrapolated to the CBS limit. The parameters a_i, D, R_e and γ_i are acquired from the least-square fitting process. To get an accurate data, of which the root means square error is minimized and the selected spectral constants from the fitted APEFs are in good consistent with the experimental results, so we attempt it from n = 3 to 9. Comparing with the experiment data, we find that the best favorable spectroscopic results can be obtained at n= 7. All of the fitted parameters of NS($X^2\Pi$) APEFs in where f_2, f_3, f_4 are quadratic, cubic and quartic force parameters, which can be calculated from the APEFs. A lot of

equations (6) and (7) are gathered in Table 1, while the *ab initio* and fitted CBS/USTE(Q,5) PECs are visualized in Figure 2. As is shown, the *ab initio* energies are accurately fitted with the maximum error being less than 3.0 cm^{-1}.

In order to evaluate the quality of the fitting, we must use the following formula to compute the root-mean square derivations (ΔE_{RMSD})

$$\Delta E_{RMSD} = \sqrt{\frac{1}{N}\{\sum_{i=1}^{N} V_{APEF}(i) - V_{ab}(i)^2\}}, \qquad (11)$$

where V_{APEF} is the corresponding fitting value and V_{ab} is the i-th energy of the *ab initio* computation, N is the number of fitting points (N = 98). All the results of the ΔE_{RMSD} are also presented in Table 1. The Table 1 lists the ΔE_{RMSD} of APEFs obtained from fitting the *ab initio* PECs of MRCI(Q)/AVTZ, MRCI(Q)/AVQZ, MRCI(Q)/AV5Z, MRCI(Q)/AV6Z, and the extrapolated CBS/USTE(Q,5) are 0.52929 cm^{-1} (about 0.00151 kcal/mol), 0.49679 cm^{-1} (about 0.00142 kcal/mol), 0.53734 cm^{-1} (about 0.00154 kcal/mol), 0.65595 cm^{-1} (about 0.00188 kcal/mol) and 0.59357 cm^{-1} (about 0.00170 kcal/mol), respectively. As a whole, computational fitting quality is much better than chemical accuracy (1.0 kcal/mol) [57]. So it reveals a high quality fitting process.

Figure 2: The extrapolated CBS/USTE(Q,5) PECs for NS($X^2\Pi$). The circles indicate the *ab initio* energies, while the line is from the fitted APEF.

3.2. Spectroscopic parameters

Using the APEFs obtained by fitting the PECs calculated at the MRCI(Q)/AVXZ (X=T, Q, 5 and 6) basis sets and the extrapolated CBS/USTE(Q,5) level of theory, the spectroscopic constants of NS($X^2\Pi$) are calculated. The spectroscopic parameters can be calculated with [58,62]

$$B_e = \frac{h}{8pcmR_e^2}, \qquad (12)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2 mc^2}}, \qquad (13)$$

$$a_e = \frac{6B_e^2}{\omega_e} \cdot \frac{f_3 R_e}{3f_2} + 1, \qquad (14)$$

$$\omega_e \chi_e = \frac{B_e}{8} - \frac{f_4 R_e^2}{f_2} + 15 + \left(\frac{\omega_e \alpha_e}{6R_e^2}\right)^2, \qquad (15)$$

other experimental and theoretical researches on the properties of NS($X^2\Pi$) have also been carried out. In 2013,

Gao *et al.* [39] determined the R_e, ω_e, B_e and $\omega_e\chi_e$ by MRCI+Q/AV5Z+DK calculation. By carrying out the CCSD(T) calculation with cc-pVQZ basis sets, Czernek *et al.* [36] calculated spectroscopic constants. Shi *et al.* [63] computed the PECs of the ground state and some excited states, and obtained complete spectral parameters by MRCI+Q/AV5Z+CV+DK computations. Kalcher [34] and Chong *et al.* [33] also calculated the some accurate results of the spectroscopic parameters of NS($X^2\Pi$).

Table 2 presents the results of R_e, D_e, B_e, ω_e, $\omega_e\chi_e$ and α_e of NS($X^2\Pi$) together with the other theoretical [33,34,36,39,63] and experimental [10,22,64] data. Overall, it can be concluded that the present values are in good agreement with these literature results. From Table 2, we can find that as the base set increases from AVTZ to AV6Z, the depth D_e is monotonically increasing and the deepest well depth is acquired from CBS / USTE (Q, 5) APEFs, with the difference of 0.00136 E_h from those of the AV6Z APEFs, but only differing from that of theoretical [36] value by 0.00044 E_h. The equilibrium bond length R_e is computed from CBS/USTE(Q,5) APEF to be 2.829 a_0, which is only 0.003 a_0 bigger than the experimental result [10] and 0.0030 a_0 shorter than the latest result computed by Gao *et al.* [39], it

shows a high precision. The vibrational frequency ω_e is computed to be 1218.27 cm^{-1}, giving the deviations of 0.23 cm^{-1} and 2.1 cm^{-1} from the results of experiment [22] and theoretical work [63] respectively. The spectroscopic parameters B_e from CBS/USTE(Q,5) is 0.7722 cm^{-1}, which is different to the theoretical [39] and experimental [64] results by 0.0006 cm^{-1} and 0.0001 cm^{-1}, respectively. However, the spectroscopic constants α_e and $\omega_e\chi_e$ can be affected by B_e, ω_e, and the force parameters (quadratic f_2, cubic f_3 and quartic f_4). All of these constants can induce the results of α_e and $\omega_e\chi_e$ to be larger than those of experiment [22] and theoretical work [33,34,36,39,63]. In this work, the values of the CBS/USTE (Q,5) APEF in comparison to the values of AV6Z, the deviations of R_e, D_e, B_e, ω_e, $\omega_e\chi_e$ and α_e are 0.071%, 0.752%, 0.155%, 0.296%, 0.160% and 0.275%, respectively. In addition, comparing with Ref. [63] at the CBS/USTE (Q,5) level of theory, the deviations of R_e, D_e, B_e, ω_e, $\omega_e\chi_e$ and α_e are 0.035%, 1.389%, 0.130%, 0.172%, 22.132% and 14.148%, respectively. It can be seen from the above discussion that the NS($X^2\Pi$) electronic state spectral parameters computed from the CBS/USTE(Q,5) APEF is in good consistent with other theoretical values [33,34,36,39,63] and the experimental values [10,22,64], showing high accuracy.

Table 1. Fitted parameters of NS($X^2\Pi$) APEFs in Equations (6) and (7).

Basis sets	AVTZ	AVQZ	AV5Z	AV6Z	CBS(Q,5)
R_e/a_0	2.8502	2.8376	2.8331	2.8314	2.8293
D/E_h	0.3951	0.4123	0.4202	0.4224	0.4280
a_1/a_0^{-1}	1.7310	1.7172	1.7280	1.7346	1.7242
a_2/a_0^{-2}	0.3932	0.3818	0.3926	0.3871	0.3981
a_3/a_0^{-3}	1.3562	1.2972	1.2512	1.2168	1.2352
a_4/a_0^{-4}	-0.2385	-0.2304	-0.1981	-0.1900	-0.1837
a_5/a_0^{-5}	0.3136	0.3100	0.2842	0.2686	0.2799
a_6/a_0^{-6}	-0.1816	-0.1649	-0.1489	-0.1387	-0.1442
a_7/a_0^{-7}	0.0381	0.0342	0.0319	0.0304	0.0313
γ_0/a_0^{-1}	1.2263	1.2169	1.2331	1.2398	1.2346
γ_1/a_0^{-1}	1.1796	1.2064	1.1852	1.1808	1.1864
γ_2/a_0^{-1}	0.6219	0.5884	0.5702	0.5541	0.5623
$C_6/E_h a_0^{-6}$	71.388	71.451	69.870	70.046	68.285
$C_8/E_h a_0^{-8}$	1688.29	1689.79	1652.40	1656.54	1614.90
$C_{10}/E_h a_0^{-10}$	52305.1	52352.6	51193.1	51321.5	50031.4
$\Delta E_{RMSD}/\text{cm}^{-1}$	0.52929	0.49679	0.53734	0.65595	0.59357

3.3. Vibrational manifolds

In order to acquire the vibrational manifolds, we have to use the program Level 7.5 [65] to calculate the radial Schrödinger equation of the nuclear motion. By the influence of adiabatic approximation, the equation should be expressed as [66]
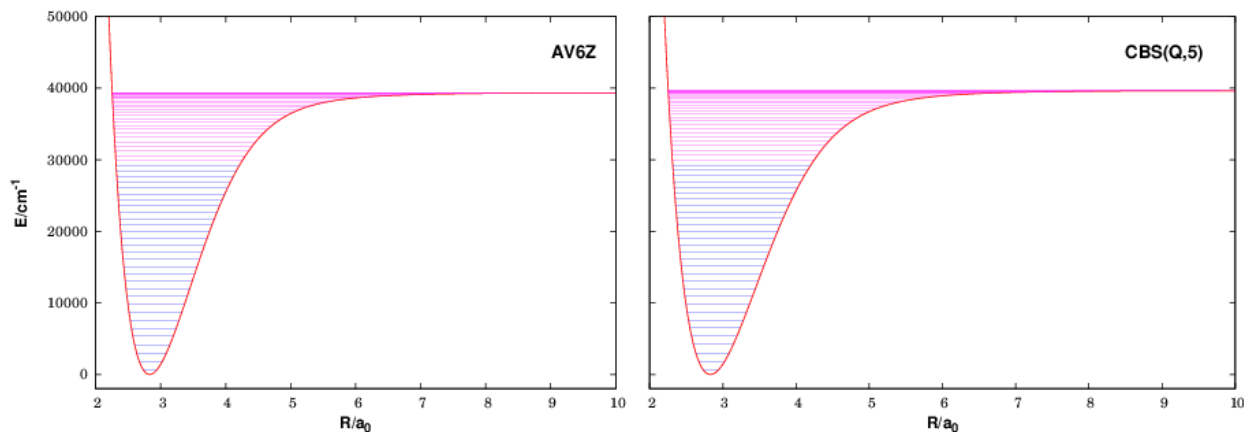
$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+\frac{\hbar^2}{2\mu r^2}J(J+1)+V(r)\right]\psi_{v,J}(r)=E_{v,J}\psi_{v,J}(r), \quad (16)$$

where $V(r)$ is the rotationless APEF listed in Table 1, μ is the molecule reduced mass, r is the internuclear distance of the N and S atom, $J(J+1)\cdot\hbar^2/2\mu r^2+V(r)$ is the potential, so $\psi_{v,J}(r)$

are the eigenfunctions and $E_{v,J}$ are the eigenvalues, J and v are the rotational quantum numbers and the vibrational quantum numbers, respectively. The rotational sublevel of a given vibrational level is expressed by the next power series

$$E_{v,J} = G(v) + B_v J(J+1) - D_v J(J+1)$$

$$-D_v J(J+1)^2 + H_v J(J+1)^3 + L_v J(J+1)^4$$
$$+M_v J(J+1)^5 + N_v J(J+1)^6 + O_v J(J+1)^7 \qquad (17)$$

here, $G(v)$ is the vibrational level, B_v is the inertial rotation constant and H_v, N_v, L_v, D_v, O_v and M_v are the centrifugal distortion constants.

Figure 3: A comparison of the vibrational energy spectrum for NS($X^2\Pi$). Left panel: the vibrational energy spectrum obtained from the extrapolated AV6Z. Right panel: the vibrational energy spectrum obtained from the extrapolated CBS/USTE(Q,5).

Table 2. Spectroscopic constants compared with experimental and other theoretical data for the NS($X^2\Pi$) molecule. The dissociation energies are in E_h, equilibrium bond length in a_0, while ω_e, B_e, α_e, and $\omega_e\chi_e$ are in cm^{-1}.

	D_e	R_e	ω_e	B_e	α_e	$\omega_e\chi_e$
AVTZ	0.16903	2.850	1193.76	0.7609	0.00743	9.603
AVQZ	0.17599	2.838	1207.17	0.7677	0.00734	9.432
AV5Z	0.17844	2.833	1212.90	0.7701	0.00731	9.391
AV6Z	0.17940	2.831	1214.67	0.7710	0.00730	9.368
CBS(Q,5)	0.18076	2.829	1218.27	0.7722	0.00728	9.353
Theory[39]	–	2.832	1220.9	0.7716	–	7.63
Theory[34]	–	2.847	1202.4	0.742	–	7.24
Theory[63]	0.17825	2.828	1216.17	0.7732	0.00625	7.283
Theory[33]	–	2.827	1279	–	0.00642	7.69
Theory[36]	0.18032	2.840	1229.36	–	0.00536	8.230
Experiment[64]	–	2.824	1218.7	0.7723	–	–
Experiment	–	2.826[10]	1218.5[22]	0.773[10]	–	7.24[22]

By calculating Equation (16) with the Numerov approach, a complete set of vibrational states for NS($X^2\Pi$) when the rotational quantum number $J=0$ is acquired. Table 3 lists the inertial rotation constants B_v, the vibrational levels $G(v)$ and the classical turning points (R_{max} and R_{min}) computed from both the AV6Z and CBS/USTE(Q,5) APEFs for NS($X^2\Pi$). Because the table cannot be too long, we only listed the first 21 vibrational levels. By comparison, the

CBS/USTE(Q,5) APEF produces a bit larger vibrational levels $G(v)$ than AV6Z APEF, and the deviation becomes more obvious as the number of vibrations v increases. By comparison, CBS / USTE (Q, 5) APEF a higher vibration level $G(v)$ than AV6Z APEF, and the deviation becomes more pronounced as. In detail, the deviations of the CBS/USTE(Q,5) APEF results from the AV6Z ones are only by 1.803 cm^{-1} (0.297%) and 70.513 cm^{-1} (0.323%) for $v=0$ and

20, respectively. The maximal difference for the B_v, R_{min} and R_{max} is found at $v = 20$ with the value of 1.369×10^{-3} cm^{-1}, 1.66×10^{-3} a_0 and 4.39×10^{-3} a_0, respectively. The inertial rotation constants and classical turning points difference at 10^{-3} magnitude, showing a high quality.

In addition, we also plot the vibrational energy spectrum using AV6Z and CBS/USTE(Q,5) APEFs for NS(X$^2\Pi$). In the Figure 3, left panel presents 59 vibrational states obtained from the AV6Z APEF, and right panel presents 60 vibrational states obtained from the CBS/USTE(Q,5) APEF. It can be seen from the Figure 3, with the increase of vibrational quantum number, vibration energy spectrum gradually converge to dissociation energy, these data are in good consistent with the physical meaning of the diatomic molecular vibrational spectroscopy.

Table 4 and Table 5 present the other six centrifugal distortion constants H_v, N_v, L_v, D_v, O_v and M_v obtained from the CBS/USTE(Q,5) and AV6Z APEFs, there are small deviation between them. It is with regret that theory data or experiment results have not been acquired in other literature on the vibrational levels, inertial rotation constants, centrifugal distortion constants and classical turning points. So, we cannot compare directly, but based on the high precision fitting of these APEFs, and the admirable accordance between the calculated spectral constants and the effective results recorded in the other literature, it can be believed that the results listed in Tables 3-5 are precise and credible. Moreover, we can also draw a conclusion that the APEF acquired at the CBS/USTE(Q,5) can represent the interaction potential of the NS(X$^2\Pi$).

Table 3. Vibrational levels $G(v)$ (in cm^{-1}), classical turning points (in a_0), and rotational constant B_v (in cm^{-1}) of the first 21 vibrational states for NS(X$^2\Pi$) when J = 0, predicted by the CBS/USTE(Q,5) and AV6Z APEFs.

v	CBS/USTE(Q, 5)				AV6Z			
	$G(v)$	R_{min}	R_{max}	B_v	$G(v)$	R_{min}	R_{max}	B_v
0	607.389	2.73395	2.93594	0.769131	605.586	2.73590	2.93819	0.767988
1	1811.217	2.67046	3.02206	0.762894	1805.863	2.67233	3.02445	0.761748
2	3000.521	2.62960	3.08582	0.756641	2991.662	2.63143	3.08832	0.755492
3	4175.281	2.59801	3.14059	0.750370	4162.956	2.59980	3.14319	0.749217
4	5335.465	2.57181	3.19025	0.744078	5319.713	2.57358	3.19294	0.742923
5	6481.032	2.54926	3.23658	0.737762	6461.886	2.55100	3.23935	0.736604
6	7611.934	2.52936	3.28057	0.731420	7589.420	2.53109	3.28341	0.730258
7	8728.109	2.51151	3.32283	0.725048	8702.248	2.51323	3.32576	0.723882
8	9829.482	2.49531	3.36380	0.718641	9800.291	2.49701	3.36681	0.717470
9	10915.968	2.48046	3.40378	0.712196	10883.455	2.48215	3.40687	0.711019
10	11987.466	2.46674	3.44300	0.705708	11951.633	2.46843	3.44618	0.704524
11	13043.862	2.45401	3.48166	0.699171	13004.705	2.45568	3.48493	0.697978
12	14085.028	2.44212	3.51989	0.692580	14042.533	2.44379	3.52326	0.691377
13	15110.817	2.43098	3.55784	0.685929	15064.967	2.43264	3.56130	0.684713
14	16121.068	2.42050	3.59560	0.679212	16071.836	2.42216	3.59917	0.677981
15	17115.606	2.41062	3.63328	0.672420	17062.957	2.41228	3.63696	0.671173
16	18094.233	2.40128	3.67097	0.665548	18038.125	2.40293	3.67477	0.664282
17	19056.737	2.39243	3.70875	0.658586	18997.122	2.39408	3.71269	0.657299
18	20002.887	2.38403	3.74671	0.651527	19939.708	2.38568	3.75078	0.650215
19	20932.433	2.37604	3.78492	0.644360	20865.623	2.37770	3.78915	0.643021
20	21845.104	2.36844	3.82347	0.637077	21774.591	2.37010	3.82786	0.635708

Table 4. Centrifugal distortion constants (in cm^{-1}) of the first 21 vibrational states for NS(X$^2\Pi$) when J = 0, calculated from CBS/USTE(Q,5) APEF.

v	$D_v/10^{-6}$	$H_v/10^{-13}$	$L_v/10^{-18}$	$M_v/10^{-23}$	$N_v/10^{-28}$	$O_v/10^{-34}$
0	1.24299	-2.53884	-3.05116	-1.28795	-0.73177	-4.76235
1	1.24705	-2.90913	-3.29196	-1.49502	-0.92323	-6.34270
2	1.25140	-3.31688	-3.58225	-1.75212	-1.15243	-7.92479
3	1.25611	-3.74946	-3.92866	-2.06422	-1.42802	-9.64582
4	1.26121	-4.27469	-4.33862	-2.43838	-1.75461	-11.09197
5	1.26677	-4.84077	-4.81967	-2.88104	-2.14381	-12.79123
6	1.27286	-5.47634	-5.38046	-3.40264	-2.60511	-13.85956
7	1.27955	-6.19058	-6.03034	-4.01368	-3.14988	-13.88967
8	1.28692	-6.99321	-6.77963	-4.72710	-3.80625	-14.25726
9	1.29504	-7.89476	-7.64095	-5.56192	-4.58056	-10.48619
10	1.30401	-8.90651	-8.62742	-6.53264	-5.52045	-11.38828
11	1.31392	-10.04093	-9.75689	-7.67511	-6.65845	-2.01917
12	1.32487	-11.31169	-11.04761	-9.01057	-8.04434	3.71789
13	1.33697	-12.73411	-12.52337	-10.58283	-9.73417	13.59304
14	1.35034	-14.32536	-14.21190	-12.43980	-11.80720	27.90463
15	1.36509	-16.10496	-16.14639	-14.64107	-14.36239	47.76954
16	1.38137	-18.09519	-18.36679	-17.26016	-17.52957	72.88072
17	1.39933	-20.32164	-20.92126	-20.38834	-21.47804	101.06647
18	1.41913	-22.81396	-23.86805	-24.13935	-26.42959	127.11226
19	1.44094	-25.60657	-27.27795	-28.65587	-32.67618	141.40816
20	1.46497	-28.73979	-31.24081	-34.15609	-40.49218	234.36432

Table 5. Centrifugal distortion constants (in cm^{-1}) of the first 21 vibrational states for NS(X$^2\Pi$) when J = 0, calculated from AV6Z APEF.

v	$D_v/10^{-6}$	$H_v/10^{-13}$	$L_v/10^{-18}$	$M_v/10^{-23}$	$N_v/10^{-28}$	$O_v/10^{-34}$
0	1.24476	-2.57946	-3.02835	-1.29047	-0.75471	-4.98066
1	1.24870	-2.94980	-3.28565	-1.51254	-0.95473	-6.60924
2	1.25296	-3.36128	-3.59418	-1.78515	-1.19221	-8.16628
3	1.25759	-3.82113	-3.96034	-2.11316	-1.47695	-9.83776
4	1.26265	-4.33703	-4.39138	-2.50330	-1.81547	-11.55639
5	1.26820	-4.91706	-4.89517	-2.96432	-2.21515	-12.65278
6	1.27431	-5.56975	-5.48001	-3.50449	-2.69180	-13.90584
7	1.28106	-6.30419	-6.15554	-4.13589	-3.26009	-15.00209
8	1.28851	-7.13011	-6.93288	-4.87471	-3.93531	-13.91457
9	1.29676	-8.05803	-7.82424	-5.73611	-4.75003	-13.12731
10	1.30588	-9.09940	-8.84469	-6.74483	-5.72806	-8.78655
11	1.31598	-10.26685	-10.01162	-7.92907	-6.90665	1.91232
12	1.32716	-11.57436	-11.34465	-9.31465	-8.35762	8.23146
13	1.33952	-13.03765	-12.86885	-10.94832	-10.13104	18.64204
14	1.35319	-14.67447	-14.61343	-12.88085	-12.31178	33.15929
15	1.36829	-16.50502	-16.61345	-15.17563	-15.00364	53.77830
16	1.38497	-18.55245	-18.91107	-17.91023	-18.35046	77.54117
17	1.40336	-20.84348	-21.55719	-21.18189	-22.53263	102.36643
18	1.42365	-23.40905	-24.61350	-25.11182	-27.78937	121.94716
19	1.44600	-26.28519	-28.15612	-29.86829	-34.44275	151.62144
20	1.47064	-29.51437	-32.27681	-35.63405	-42.78232	197.99769

4. Conclusions

The PECs of NS(X$^2\Pi$) are modeled by fitting *ab initio* energies calculated using the CASSCF as the reference wave function followed by the MRCI(Q) approach in combination with a

series of correlation-consistent AVXZ (X = T, Q, 5 and 6) basis sets. In order to obtain PECs with high accuracy, PECs calculated with aug-cc-pV(Q,5)Z basis sets are extrapolated to the CBS limit. The so-obtained PECs are subsequently fitted to APEFs using the EHFACE model, used to determine the spectroscopic parameters, D_e, R_e, ω_e, B_e, α_e and $\omega_e\chi_e$. By comparison with the available experiments, the results obtained from the CBS/USTE(Q,5) and AV6Z APEF exhibit high accuracy. Then, by numerically solving the radial Schrödinger equation of nuclear motion using the Numerov method, the complete set of vibrational states has been calculated when J=0. For each vibrational state, one vibrational level and its corresponding classical turning points, one inertial rotation constant and six centrifugal distortion constants are also produced. As a whole, the present results provide a more accurate and complete investigations of the spectroscopic parameters and vibrational manifolds of the NS($X^2\Pi$) molecule.

Acknowledgements

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