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# Theoretical study of the spectroscopy and radiative transition properties of NS



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#### 1. Introduction

The NS molecule possesses a large number of valence and Rydberg states, the low-lying states  $X^2\Pi$ ,  $B^2\Pi$ ,  $B'^2\Sigma^+$ ,  $A^2\Delta$ ,  $G^2\Sigma^-$ ,  $C^2\Sigma^+$ ,  $H^2\Pi$ ,  $I^2\Sigma^-$ ,  $E^2\Pi$ ,  $J^2\Sigma^+$  and  $F^2\Delta$  all have been observed by Jenouvrier and his co-workers [1–3], in which the C, E, J and F states were characterized as Rydberg states. As early as 1932, the two bands of A-X and C-Xsystems between 2300 and 2700 Å in emission of the radical NS were discovered by Fowler and Bakker [4]. In 1951, Zeeman [5] measured the (0, 0) and  $(0, 1) \gamma$  bands, and determined the coupling constant A (223.03  $\text{cm}^{-1}$ ) of the ground state  $(X^2\Pi)$ . Since 1966, there have been a number of experiments [6-20], in which the accuracy of the spectroscopic parameters have been improved. The first Rydberg  ${}^{1}\Sigma^{+}$  state of NS is  $C^{2}\Sigma^{+}$  ( $2\pi^{4}s$ ), which has a weaker predissociation character. The radiative lifetime of the v' = 0 level of  $C^2 \Sigma^+$  was measured to be 6.5 ns by Silvers et al. [21]. Recently, Wang et al. [22] reported the resonance-enhanced multiphoton ionization spectroscopy

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#### ABSTRACT

The low-lying electronic states ( $X^2\Pi$ ,  $a^4\Pi$ ,  $b^4\Sigma^-$ ,  $B^2\Pi$ ,  $1^2\Phi$ ,  $A^2\Delta$  and  $B'^2\Sigma^+$ ) of the NS molecule are computed at the AV5Z/CASSCF/MRCI+Q+DK level of theory. The potential energy curves are presented for these states; the corresponding spectroscopic constants are reported. Electronic transition moment functions, Einstein coefficients, Franck-Condon factors and radiative lifetimes for the  $B^2\Pi - X^2\Pi$ ,  $B'^2\Sigma^+ - X^2\Pi$  and  $A^2\Delta - X^2\Pi$  system have been calculated. The F–C factors of the  $B^2\Pi$  are in good agreement with the corresponding RKR data. The  $B'^2\Sigma^+$  state possesses a barrier in the potential energy curve, located at about 2.16 Å. The height of the barrier is predicted to be 7890 cm<sup>-1</sup>.

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on the  $B'^{2}\Sigma^{+}$  and  $B^{2}\Pi$  states of NS and obtained exhaustive spectroscopic constants of both the  $X^{2}\Pi$  ground state and the  $B'^{2}\Sigma^{+}$  excited state.

Early ab initio calculations on the valence states of NS were undertaken by Bialski and Grein [15] using minimal basis full-valence-CI techniques. Lie et al. [23] calculated the low-lying valence and Rydberg states of NS using configuration-interaction method. A shortcoming of the work by Lie et al. is their inability to obtain the  $B^{\prime 2}\Sigma^{+}$  state, which has been observed in experiments. The  $B'^2\Sigma^+$  state has been classified experimentally as a valence state [11,13]. This state has been well described by Karna and Grein [24,25]. From then on, several studies [26–30] have been performed on the low-lying states and Rydberg states of NS. Very recently, the spin-orbit splitting values of the  $X^2\Pi$ ,  $a^4\Pi$ ,  $B^2\Pi$  and  $H^2\Pi$  of NS were computed by Shi et al. [31], in which the core-valence correlation and relativistic corrections were taken into account. Most previous theoretical studies focused on the predissociation of the  $C^2\Sigma^+$  state, and did not study these transitions from low-lying bound excited states (except for the  $C^2\Sigma^+$  state) to the ground state  $X^2\Pi$ .

In order to resolve the abovementioned radiative transition probabilities of the low-lying excited states ( $B^2\Pi$ ,  $B'^{2}\Sigma^{+}$  and  $A^{2}\Delta$ ), and to establish for the three band system  $B^{2}\Pi - X^{2}\Pi$ ,  $B'^{2}\Sigma^{+} - X^{2}\Pi$  and  $A^{2}\Delta - X^{2}\Pi$  reliable radiative transition probabilities and lifetimes, we calculated potential energy curves (PECs) of low-lying electronic states and transition dipole moments (TDMs). Based on the obtained PECs, the spectroscopic constants, the Einstein coefficient and the Franck–Condon (FC) factors of the transitions from the low-lying excited states to the ground state are also calculated. Based on the above calculations, the radiative lifetimes of the  $B^{2}\Pi$ ,  $B'^{2}\Sigma^{+}$  and  $A^{2}\Delta$  are theoretically predicted.

#### 2. Computational details

In this work, our main concern is a high-level description of the potential energy curves of low-lying electronic states of the NS molecule, and the transition dipole moment between them. Scalar relativistic effects are taken into account through the second-order Douglas-Kroll and the Cowan-Griffin operator. These tested results are summarized in Supplementary Table 1. The present electronic structure calculations are performed using the Molpro 2009.1 program [32]. In these calculations, the correlation consistent polarized quintuple zeta (aug-cc-pV5Z) basis set [33,34] is chosen for both atoms. The state-averaged complete active space self-consistent field (SA-CASSCF) [35,36] is performed first to generate the optimized molecular orbitals. The active space is CAS (11, 8), i.e., there are eleven electrons distributed in all possible ways in the 2s and 2p orbitals of nitrogen and the 3s and 3p orbitals of sulfur. Dynamical electronic correction is obtained by the internally contracted multi-reference configuration interaction (icMRCI) method with the Davidson correction (+O) [37–39]. The electronic correlation energy can be well extrapolated in single-reference cases by

$$E_{\infty} = E_X + A X^{-3},\tag{1}$$

where *X* is the cardinal number of the basis set, i.e. X=4, 5 for aug-cc-pVQZ and aug-cc-pV5Z, respectively.  $E_X$  is the correlation energy calculated by the AVXZ basis set, and  $E_{\infty}$  is the correlation energy extrapolated to the complete basis set (CBS) limit. Halkier et al. [40] derived the following formula:

$$\Delta E_{\infty} = \frac{\Delta E_X X^3 - \Delta E_Y Y^3}{X^3 - Y^3},\tag{2}$$

with *X* and *Y* being the two cardinal numbers. In order to obtain extrapolated total energies, the reference energy has to be considered as well. The computed results are listed in Supplementary Table 1.

These calculations were carried out in the  $C_{2\nu}$  point group, and one  ${}^{2}A_{1}$ , three  ${}^{2}B_{1}$ , three  ${}^{2}B_{2}$ , one  ${}^{4}B_{1}$ , one  ${}^{4}B_{2}$ , one  ${}^{2}A_{2}$ , and one  ${}^{4}A_{2}$  states have been averaged together using the CASSCF averaging procedure implemented in Molpro. These low-lying electronic states correlating with the first dissociation channel (N( ${}^{4}S_{u}$ )+S( ${}^{3}P_{g}$ )), namely, one  ${}^{2}\Pi$ , one  ${}^{4}\Pi$ , one  ${}^{2}\Sigma^{+}$  states, and one state correlating with the second dissociation channel (N( ${}^{4}S_{u}$ )+S( ${}^{1}D_{g}$ )), namely,  ${}^{4}\Sigma^{-}$  state, and three states correlating with the third dissociation channel (N( ${}^{2}D_{u}$ )+S( ${}^{3}P_{g}$ )), namely, one  ${}^{2}\Pi$ , one  ${}^{2}\Delta$  states.

The nuclear motion problem was solved using Le Roy's numerical integration LEVEL8.0 [41] procedure. The corresponding spectroscopic parameters, FCs, Einstein coefficient and radiative lifetime were also calculated. The spectroscopic constants obtained by the extrapolation with and without Davidson correction and valence electronic correlating and scalar relativistic effects are summarized in Supplementary Table 1.

#### 3. Results and discussion

#### 3.1. Spectroscopic constants

As seen in Supplementary Table 1, the Davidson corrections shorten the  $R_e$  for the selected electronic states except for the ground state  $X^2\Pi$ , lower the  $T_e$  for all the electronic states and increase the  $\omega_e$  for the  $a^4\Pi$ ,  $B^2\Pi$ ,  $b^4\Sigma^$ and  $1^2\Phi$  except for the  $X^2\Pi$  and  $A^2\Delta$ , and lower the  $\omega_{e\chi e}$  for the  $X^2\Pi$ ,  $a^4\Pi$ ,  $b^4\Sigma^-$  and  $A^2\Delta$  expect for the  $B^2\Pi$  and  $1^2\Phi$ . In detail, the difference of the  $R_e$  within 0.006 Å for all the electronic states; the shifts of the  $T_e$  are by 42 to 684 cm<sup>-1</sup>; the shifts of the  $\omega_e$  are by 3.1 to 16.3 cm<sup>-1</sup>. On the whole, the effect on the  $T_e$  by the Davidson corrections is more pronounced than that on the  $R_e$ ,  $\omega_e$  and  $\omega_{e\chi e}$ .

As seen in Supplementary Table 1, the addition of dynamical correlation made the calculated  $R_e$  results about 0.02–0.049 Å smaller than without the correction at AV52/ MRCI-DK theoretical level. The shifts of the  $T_e$  are by 136.7 to 1789 cm<sup>-1</sup> when dynamical correlation was taken into account. Comparing with the Davidson corrections, the effect on the spectroscopic constants of the NS molecule by dynamical correction is more significant.

Estimates for the CBS have been obtained by extrapolating the AVQZ and AV5Z correlation energies. Supplementary Table 1 clearly shows the results are similar between the AV5Z-DK/MRCI and the CBS results.

The different approximations of scalar relativistic effects (the second-order Douglas-Kroll and the Cowan-Griffin operator) were tested. The results are summarized in Supplementary Table 1. On the whole, one can find that the spectroscopic constants determined by the AV5Z-DK/ MRCI+Q computations are closer to the AV5Z-CG/MRCI+Q computations. For example, the  $R_e$  obtained by the AV5Z-DK/MRCI+O calculations deviate from the experimental data [5] by only 0.003 Å for the  $X^2\Pi$ , whereas the  $R_e$ obtained by the AV5Z-CG/MRCI+Q calculations deviate from the experimental data by only 0.005 Å for the  $X^2\Pi$ . The  $\omega_e$ obtained by the AV5Z-DK/MRCI+O calculations deviate from the experimental data by only 2.4 cm<sup>-1</sup> for the  $X^2\Pi$ , whereas the  $\omega_e$  obtained by the AV5Z-CG/MRCI+Q calculations deviate from the experimental data by only 2.1 cm<sup>-1</sup> for the  $X^2\Pi$ .

### 3.2. Potential energy curves and their spectroscopic properties

Presently, the doublet and quartet bound electronic states correlating to the three lowest dissociation limits of NS, i.e.,  $N(^4S_u)+S(^3P_g)$ ,  $N(^4S_u)+S(^1D_g)$  and  $N(^2D_u)+S(^3P_g)$ , are investigated with the MRCI-DK+Q method using aug-cc-pV5Z basis set. The present work studies a selected



Fig. 1. MRCI+Q survey of the ground and low-lying A-S electronic states with doublet and quartet spin multiplicities of the NS molecule using an AV5Z basis set.

number of low-lying states of the NS molecule. (Only three of the five possible resulting from  $2\pi \rightarrow 3\pi$  excitation, two out of four possible for  $7\sigma \rightarrow 3\pi$  transitions plus the  $3\pi \rightarrow 8\sigma$  $(B'^{2}\Sigma^{+})$ , and that no special search is made for Rydberg states.) The PECs for the 7  $\Lambda$ -S electronic states are shown in Fig. 1. Table 1 list the computed spectroscopic constants of NS, including the adiabatic transition energies  $T_{e}$ , the harmonic vibrational frequencies  $\omega_e$ , the anharmonic terms  $\omega_{e\chi_e}$ , the equilibrium rotational constants  $B_e$  and the equilibrium internuclear distance  $R_e$ . Table 1 also lists the dominant configurations for calculated states at their respective R<sub>e</sub> or around 1.48 Å for weakly bounded state  $(B^{2}\Sigma^{+})$ . For comparison, we also list the results of previous experimental and theoretical studies [3,5,10,15,17,22,23-28,30,31,42,43] where available. It is noted that the *ab* initio potentials calculated using a AV5Z basis show good agreement with the experimental data which indicates that the AV5Z basis is sufficient to reproduce experimental results to an excellent degree of accuracy.

As shown in Fig. 1, five doublet states  $(X^2\Pi, B^2\Pi, B'^2\Sigma^+,$  $A^2\Delta$  and  $1^2\Phi$ ) and two quartet states ( $a^4\Pi$  and  $b^4\Sigma^-$ ) are correlated to the first three dissociation limits of NS. The ground state  $X^2\Pi$  has a deep potential well in PEC, and the calculated bond length is 1.498 Å; the  $a^4\Pi$ ,  $B^2\Pi$  and  $1^2\Phi$ states have similar internuclear distances, this is probably related to the same electronic configuration of the three states, which is mainly described by  $6\sigma^2 7\sigma^2 2\pi^3 3\pi^2$  at around 1.7 Å; the  $b^4\Sigma^-$  and  $A^2\Delta$  states have the same main configurations  $6\sigma^2 7\sigma 2\pi^4 3\pi^2$ ; the  $B'^2 \Sigma^+$  state is a weakly bounded valence state at  $R_e = 1.4816$  Å but turns to be repulsive at around 2.16 Å, though the  $R_e$  is smaller than the ground states. Our calculated spectroscopic constants of the low-lying valence states are in good agreement with previous available experimental [3,5,17,22,43] and theoretical results [3,15,23-28,30-31,42], as shown in Table 1.

As expected, the ground state of NS is  $X^2\Pi$  with  $R_e = 1.498$  Å,  $\omega_e = 1220.9 \text{ cm}^{-1}$  and  $\omega_{e\chi e} = 7.63 \text{ cm}^{-1}$ . Our calculated results are in good agreement with the theoretical results of Ref. [31]. It is mainly described by an open shell configuration  $6\sigma^27\sigma^22\pi^43\pi^1$  ( $c^2=0.91$ ). The differences between our calculations and the experimental data [5,17] are 0.003 Å, 2.4 cm<sup>-1</sup>, 0.39 cm<sup>-1</sup> and 0.0021 cm<sup>-1</sup>, for  $R_e$ ,  $\omega_{e\chi}$  and  $B_e$ , respectively.

The next prominent A-S state of NS is  $a^4\Pi$  state, which has the same dominating configurations as those to the  $B^2\Pi$  and  $1^2\Phi$  states (see Table 1). Our computed NS ( $a^4\Pi$ ) equilibrium distance is  $R_e$ =1.723 Å. It agrees to within 0.027 Å with previous experimental data [3] and theoretical values [25,31] (see Table 1 for more details). For the  $B^2\Pi$  and  $1^2\Phi$  states, the computed equilibrium distances are 1.700 Å and 1.702 Å, the corresponding experimental data [10] and theoretical value [25] are 1.703 Å and 1.723 Å, respectively. The  $a^4\Pi$  state is lying 24,524 cm<sup>-1</sup> above the ground state, while for the  $B^2\Pi$  and  $1^2\Phi$  states, the adiabatic transition energies  $T_e$  are 30,198.2 cm<sup>-1</sup> and 36,816 cm<sup>-1</sup>, respectively. The corresponding experimental and theoretical data [3,10,23] are ~27,005 cm<sup>-1</sup>, 30,326.4 cm<sup>-1</sup> and 37,117 cm<sup>-1</sup>.

The valence excited state  $b^4\Sigma^-$  is lying 30,086 cm<sup>-1</sup> above the ground state. There are no experimental data available for comparison. The equilibrium internuclear distance for the  $b^4\Sigma^-$  state is 1.579 Å, to be compared with the other theoretical value of 1.572 Å [25]. The other spectroscopic parameters ( $\omega_e$  and  $B_e$ ) are all in good agreement with previous available theoretical results [15,23,25], as shown in Table 1. The  $A^2\Delta$  state is lying 40,399 cm<sup>-1</sup> above the ground state. As seen from Table 1, the  $b^4\Sigma^-$  and  $A^2\Delta$  states have almost equal spectroscopic parameters, and the calculated results of the  $A^2\Delta$  state are in good agreement with the experimental data [43].

For the  $B'^2\Sigma^+$  state, it possesses a barrier in the potential energy curves, located at about 2.16 Å. The computed height

#### Table 1

Comparison of the spectroscopic constants of the NS molecule with available experimental results and other theoretical ones.

State	$T_{e}  ({\rm cm}^{-1})$	$R_e$ (Å)	$\omega_e (\mathrm{cm}^{-1})$	$\omega_{e\chi e}$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	Main CSF at $R_e^{a}(\%)$
<i>Х</i> <sup>2</sup> П	0	1.498	1220.9	7.63	0.7715	$6\sigma^2 7\sigma^2 2\pi^4 3\pi^1(91)$
Calc. [25]	0	1.515	1220.5	-	0.7542	
Calc. [26]	0	1.506	1202.4	7.24	-	
Calc. [27]	0	1.494	1204	6.8	-	
Calc. [28]	0	1.502	1229.4	8.23	-	
Calc. [30]	0	1.501	1203.4	6.24	0.767	
Calc. [31]	0	1.496	1216.2	7.28	0.7732	
Calc. [42]	0	1.495	1279	7.69	-	
Exp. [43]	0	1.494	1218.7	-	0.7723	
Exp.	0	1.495 [5]	1218.5 ± 2.5 [17]	7.24 ± 0.34 [17]	0.7736 [5]	
$B^2\Pi$	30,198.2	1.700	805	3.72	0.5987	$6\sigma^2 7\sigma^2 2\pi^3 3\pi^2(91) 2\pi \to 3\pi$
Calc. [25]	31,375.0	1.698	794.7	-	0.6002	
Calc. [31]	30,245.1	1.700	797.6	3.72	0.5992	
Calc. [23]	31,697.6	1.753	428	-	-	
Exp. [10]	30,328.5 <sup>b</sup>	1.703 <sup>b</sup>	800 <sup>b</sup>	3.72 <sup>b</sup>	0.5964 <sup>b</sup>	
Exp. [43]	30,326.4	1.697	797.3	-	0.5962	
$1^2 \Phi$	36,816	1.702	785	5.24	0.5978	$6\sigma^2 7\sigma^2 2\pi^3 3\pi^2(95) 2\pi \to 3\pi$
Calc. [23]	37,117	1.757	1156	-	-	
Calc. [25]	38,473	1.723	820.7	-	0.5828	
$a^4\Pi$	24,524	1.723	751	6	0.5832	$6\sigma^2 7\sigma^2 2\pi^3 3\pi^2(90) \ 2\pi \to 3\pi$
Calc. [25]	22,584	1.734	782.1	-	0.5757	
Calc. [31]	24,542	1.723	736.0	5.7	0.5833	
Exp. [3]	$\sim$ 27,005	1.75	$\sim$ 760	$\sim 4$	$\sim 0.56$	
$A^2\Delta$	40,399	1.578	950.1	7.43	0.6954	$6\sigma^2 7\sigma 2\pi^4 3\pi^2 (89) 7\sigma \rightarrow 3\pi$
Calc. [23]	40,381	1.583	1162	-	-	
Calc. [24]	-	1.600	937.0	-	0.6761	
Calc. [25]	41,054	1.589	926.3	-	0.6849	
Exp. [43]	40,005	1.589	943.9	-	0.6850	
$b^4\Sigma^-$	30,086	1.579	948.7	8.45	0.6943	$6\sigma^2 7\sigma 2\pi^4 3\pi^2(93) 7\sigma \rightarrow 3\pi$
Calc. [15]	23,700	1.79	$\sim 950$	-	-	
Calc. [23]	29,731	1.616	952	-	-	
Calc. [25]	30,246	1.572	886.9	-	0.7004	
$B'^2\Sigma^+$	36,597.9	1.4816	1048.2	30.16	0.7903	$6\sigma^2 7\sigma^2 2\pi^4 8\sigma(86) \ 3\pi \rightarrow 8\sigma$
Calc. [3]	35,624.3	1.4747	1091.5	24.5	0.7945	
Calc. [25]	-	1.480	1189.3	-	0.7898	
Exp. [22]	36,224.5	1.4699	1102.8	29.95	0.8005	
Exp. [43]	36,255	1.49	1060	-	0.78	

<sup>a</sup> Excitations given relative to configuration  $(1\sigma-5\sigma)^2 1\pi^4$ .

<sup>b</sup> Average value.

of the barrier is about 7890 cm<sup>-1</sup>. The computed  $R_e$  is 1.4816 Å for the  $B'^{2}\Sigma^{+}$ . The  $B'^{2}\Sigma^{+}$  state locates at 36,597.9 cm<sup>-1</sup> above the ground state, which reasonably agrees with the experimental value of 36,255 cm<sup>-1</sup> [43] and 36,224.5 cm<sup>-1</sup> [22]. A smaller theoretical value of 35,624.3 cm<sup>-1</sup> has been given by Jenouvrier et al. [3]. The other computed spectroscopic constants ( $\omega_{e}$ ,  $\omega_{e\chi e}$  and  $B_e$ ) of the  $B'^{2}\Sigma^{+}$  state are also in good agreement with previous available experimental [22,43] and theoretical results [3], as shown in Table 1.

## 3.3. Electronic transition dipole moments and radiative lifetimes

Three dipole-allowed transitions are computed from the MRDCI results of NS. No experimental or theoretical data are known so far in this regard. We have considered transitions from three doublet states ( $B^2\Pi$ ,  $B'^2\Sigma^+$  and  $A^2\Delta$ ) to the ground state  $X^2\Pi$ . The calculated transition moments of the three transitions are plotted as a function of the internuclear distance (Fig. 2). The  $B'^2\Sigma^+ - X^2\Pi$  transition dipole moment starts from large negative values then decreases rapidly between 1.7 and 4.5 Å and finally becomes zero value at larger distance. The shape of the  $B^2\Pi - X^2\Pi$  transition dipole moment is like the usual PECs, in which there is a negative minimal value. The  $A^2\Delta - X^2\Pi$  transition is very weak, within the range of -0.2 to -0.2 Debye. There are no available experimental data and theoretical calculations for comparison. Transitions probabilities of these dipole-allowed transitions and radiative lifetime of the three states are estimated (Table 2). The radiative lifetimes are calculated only at the first six vibrational levels (v'=0-5).

The radiative lifetime for a given vibrational level v' can be obtained by the following formula [44,45]:

$$\tau_{v'} = (A_{v'})^{-1} = \left[\sum_{v',j',j''} 3.1361891 \times 10^{-7} \frac{S(j',j'')}{2j'+1} \nu^3 \left| \langle \Psi_{v',j'} \middle| M(r) \middle| \Psi_{v'',j''} \right|^2 \right]^{-1}$$

Here  $A_{v'}$  has units  $s^{-1}$ , M(r) is the dipole moment (or transition dipole) function in units debye, v the emission frequency in cm<sup>-1</sup>, S(J', J'') the Hönl–London rotational intensity factor and  $\Psi_{v'J'}$  and  $\Psi_{v'J'}$  are the unit normalized initial and final state wave functions.



**Fig. 2.** Transition dipole moments between the ground  $X^2\Pi$  and excited states of NS molecule.

 Table 2

 Radiative lifetime of transitions at different vibrational levels.

Transition	Radiativ	Radiative lifetimes (µs)							
	<i>v</i> ′=0	v' = 1	<i>v</i> ′=2	<i>v</i> ′=3	v'=4	v'=5			
$\begin{array}{c} B^{2}\Pi - X^{2}\Pi \\ B'^{2}\Sigma^{+} - X^{2}\Pi \\ A^{2}\Delta - X^{2}\Pi \end{array}$	3.58 4.61 14.93	3.57 4.72 15.38	3.57 4.88 15.63	3.46 ~ 16.67	3.61 5.38 16.95	3.79 5.78 17.24			

The radiative lifetime of the  $B^2\Pi$  state is computed to be 3.46–3.79 µs for the first six vibrational levels (v'=0-5), which is about three times the experimental lifetime of  $\sim 1$  µs. The corresponding experimental data [20] are 1.04 ± 0.10 µs, 1.00 ± 0.10 µs and 0.98 ± 0.10 µs for v'=0, 1 and 6, respectively. The radiative lifetime of the  $B^2\Pi$  state is known to be 1.01–1.29 µs for v'=6-12 [46]. The  $B'^2\Sigma^+$ – $X^2\Pi$  transition has weak strength in spite of its sound F–C factor [46]. The radiative lifetime of the  $B'^2\Sigma^+$  state is estimated to range from 4.61 to 5.78 µs for the first six vibrational levels (v'=0-5), and there are no available experimental or other theoretical data for comparison. The radiative lifetime of  $A^2\Delta$  is calculated to be 14.93 µs at v'=0, and the theoretical calculations predict increasing lifetimes with increasing v'.

The FCs of transitions from the  $B^2\Pi$ ,  $B'^2\Sigma^+$  and  $A^2\Delta$  states to the ground state  $X^2\Pi$  were also evaluated by the LEVEL program [41]. The FCs and Einstein coefficient of the  $B^2\Pi$ ,  $B'^2\Sigma^+$  and  $A^2\Delta$  states are given in Tables 2–4 of the electronic supplementary information (ESI).

#### 4. Conclusion

Low-lying electronic states of the NS radical have been studied by using ab initio based MRCI+Q+DK method with all-electronic aug-cc-pV5Z basis set. The scalar relativity correction is taken into account by utilizing the secondorder one-electron Douglas-Kroll-Hess method.

Based on the PECs, the spectroscopic constants of the low-lying electronic states are derived by solving the corresponding nuclear Schrödinger equations, which are in good agreement with previous available experimental and theoretical results. It is noted that the  $B'^2\Sigma^+$  state possesses a barrier in the potential energy curve, located at about 2.16 Å. The height of the barrier is predicted to be 7890 cm<sup>-1</sup>.

The allowed transition moments of the  $B^2\Pi$ ,  $B'^2\Sigma^+$  and  $A^2\Delta$  states to the ground state  $X^2\Pi$  were studied, and the lifetimes of the lowest six vibrational levels of the three states were evaluated. The radiative lifetime of the  $B^2\Pi$  state is computed to be 3.46–3.79 µs for the first six vibrational levels (v'=0-5), and the corresponding experimental values are about 1 µs. The FCs of the  $B^2\Pi$  is in good agreement with the RKR data.

#### Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j. jqsrt.2013.06.014.

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