

Accurate *ab initio*-based potential energy curve and spectroscopic properties of NO($X^2\Pi$) via extrapolation to the complete basis set limit

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Abstract. The potential energy curves (PECs) of NO ($X^2\Pi$) have been studied employing a multi-reference configuration interaction method with the Davidson correction and with a series of Dunning's correlation-consistent basis sets: aug-c.c.-pvxz($x=T, Q, 5$ and 6). Then computed PECs are extrapolated to the complete basis set limit. PECs are used to reduce the analytical potential energy functions (APEFs), accurate extended Hartree-Fork methods have been used to investigate electronic structure spectroscopy. Through the use of the extended Hartree-Fock approximate correlation energy method to fit APEF, we can calculate the spectroscopic parameters, consisting with the experimental and theoretical results, and we can also get the vibrational energy levels, classical turning points, centrifugal distortion constants and inertial rotation. Our calculations are sufficient to close into experimental data from other reference, so the results can supply a useful reference for future experiments.

1. Introduction

Exporting from a theoretical perspective of diatomic molecular potential energy functions have been the most important research topics [1]. According to Diatomic molecule potential energy function [2]. Nitric oxide (NO) is an environmental pollutant, main air pollution, acid rain, ozone has a big influence on human health. From the perspective of the potential energy function study on the ground state of NO [3,4] and also study on its special structure, there are many important physiological and environmental properties [5]. Numerous experimental and theoretical investigations have been performed on HNO and NO. Started in 1958 by Dalby's investigations using gas phase photolysis technique [6]. In order to determine the transition moment, the transition moment functions, Einstein A coefficients, and radiative lifetimes of NO were calculated employing internally contracted MRCI of Sheehy *et al.* [7]. Luque and Crosley [8]. offered experimental determinations of transition probabilities and electronic transition moments for the $A^2\Sigma^+ - X^2\Pi$ and $D^2\Sigma^+ - X^2\Pi$ systems of NO [9]. Although there were many studies of different system of NO, and many theoretical studies have been done, it did not quantitative research useful to predict the spectral characteristics at high temperature. Spectroscopic methods detecting trace quantities of NO in the atmosphere have been proposed based on electronic excitation [5]. The band systems were observed: $A^2\Sigma^+ - X^2\Pi$ (γ system) and $B^2\Pi - X^2\Pi$ (β system) $B^2\Pi$, NO, the lowest excited doublet

valence state was found in a number of environments, including air after glows and also shock-heated air. In the $A^2\Sigma^+$ state, it is the longest wavelength of NO absorption system [10]. Studying on the accurate APEF of NO($X^2\Pi$) was rarely proposed, which is important in the dynamics calculations and spectroscopic experiments. Inspired by the above work, we are motivated to construct highly accurate APEFs and calculate more complete spectroscopic information of NO($X^2\Pi$).

In the present work, we counted the PECs of the NO($X^2\Pi$) electronic state using multi-reference configuration interaction (MRCI), through the use of the MRCI(Q) method [11]. The MRCI(Q) method and a series of correlation-consistent basis sets of Dunning and coworkers [14], namely aug-c.c.-PVXZ, indicating as AVXZ. The uniform singlet-pair and triplet-pair extrapolation (USTE) protocol [12], is employed to extrapolate the PECs computed AV(Q,5)Z to the complete basis set (CBS) limit. The whole PECs are used to infer the APEFs. Using the extended Hartree-Fork approximate correlation energy method (EHFACE) [13], the PECs have been used to fit the APEFs. Basing on the APEFs of NO($X^2\Pi$), we obtained the exact and reliable spectroscopic parameters. Solving radial Schrödinger equations of the nuclear motion, in the theory, we gained the potential at the MRCI/aug-cc-pvxz level, the complete vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants are counted when the rotational quantum number J equals zero. The present results provide more strict and complete spectroscopic information about NO($X^2\Pi$). Too little information about it can be found in the literature finishing off its vibrational manifolds. Now, even though these vibrational parameters are very useful in the rotational transition calculations. These encourage us to complete the current research. All in all, our study offer more

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detailed and precise researches on the spectroscopic information of the NO($X^2\Pi$), compared with the previous findings from data.

Articles configuration are as follows: in section 2, introduces the theoretical approaches, like what, the application of extrapolation, the *ab initio* calculations and the APEF formalism. Then, in section 3 the results and discussions are given which evaluated potential energy curves. Section 4 is the conclusion.

2. Theoretical methods

2.1 Ab initio calculations.

We use molpro 2012, which is approach to calculating [15]. As reference of the wave function we can using the full valence complete-active-space self-consistent field(CASSCF) [16], applied to many diatomic [17,18]. The MRCI(Q) method is one of the most approaches and quantum chemistry program packages. Over here we can use the MQCI approach in combination with a series of correlation-consistent basis set aug-c.c.-PVXZ (X=T, Q, 5 and 6) of Dunning and co-workers [19,20], Studing the equilibrium internuclear distances R_e and harmonic frequencies ω_e of the NO($X^2\Pi$) molecule. Furthermore, in order to obtain the PECs of NO, the potential energies of internuclear separation ranging from 1.9 to 10 a_0 are calculated. The impacts on the spectroscopic parameters by these basis sets augmented with diffuse functions, through the use of the full valence CASSCF wave function as the reference, in the current process, we put to use the C_{2v} point group symmetry, holding four representations A1, A2, B1 and B2. Nitric oxide is an open shell molecule and the electronic configuration of $X^2\Pi$ show that all the *ab initio* energies calculated at AVXZ (X=T, Q, 5, 6) basis sets. The main effects have been neglected by closed to the core orbitals in the CASSCF and not correlating them in the MRCI(Q) calculation. Both of the standard AVXZ (X=T, Q, 5 and 6), including core-polarization high-exponent functions as recommended for the second row atoms. A main reason for using the frozen core approximation is the raw *ab initio* energies calculated with relatively modest cost AV(Q,5) are subsequently extrapolated to the CBS limit, denoted as CBS/AV(Q,5)Z. The extrapolation is carried out via extrapolation of the electron correlation energies to the CBS limit and via extrapolation to the CBS limit of the CASSCF energies.

2.2 Extrapolation to the CBS limit.

The *ab initio* energies calculated in our work have been afterwards extrapolated to the CBS limit. In order to implement the extrapolation, the MRCI(Q) electronic energy can be treated in split form, written in the following form [21,22].

$$E_X = E_X^{CAS} + E_X^{dc}, \quad (1)$$

In the formula above the subscript x delegate that the energy is counted in the AVXZ and AVXdZ basis sets, and the superscripts CAS and dc delegate the complete-active space (CAS) and the dynamical correlation energies respectively.

The X=(Q,5) are employed in the present work and denoted as USTE(Q,5). The extrapolation is carried out via extrapolation of the electron dynamic correlation energy to the CBS limit, also plusing extrapolation to the CBS limit of the CASSCF energy.

The CAS energies is lack of a dynamical correlation, and then extrapolated to the CBS limit, taking the two-point extrapolation scheme proposed by Karton and Martin [23]. and validated by Varandas [21,22] for extrapolations of the CASSCF energy

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

Where $\alpha = 5.34$ is an effective decay exponent and E_X^{CAS} is the energy of when the $X \rightarrow \infty$.

The USTE protocol [24,25] has been successfully used to extrapolate the dc energies in MRCI(Q) calculations, which can be written as the follow equation.

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

As is written as the auxiliary relation

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

Here $A_5(0) = 0.0037685459$, $\alpha = -3/8$ and $c = -1.17847713$ are the universal-type parameters [24,25], therefore equation (3) can be transformed into an (E_∞, A_3) two parameter rule, which is actually used for the practical procedure of the extrapolation. The USTE extrapolation scheme has been shown to the accurate energies even when the extrapolation is carried out with the cheapest AVdZ pair [25]. To sum up, we utilized here to extrapolate the dc energies to the CBS limit for this system.

2.3 APEF of the NO ($X^2\Pi$).

The PECS of NO($X^2\Pi$) molecular, which using the EHFACE model, and is expressed as

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

The equation $V_{EHF}(R)$ and $V_{dc}(R)$ denote the extended Hartree-Fock(EHF) and two-body terms of the dynamical correlation, respectively.

The analytical function of the EHF energy term is denoted as

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

Where $\gamma = \gamma_0 + \gamma_1 \cdot \tanh(\gamma_2 \cdot r)$ with $r = R - R_e$ as the displacement of equilibrium diatomic geometry; D , $a_i (i = 1, \dots, n)$ and $\gamma_i (i = 0, 1, 2)$ are adjustable parameters to be acquired from a least-squares fitting procedure.

The latter dc energy term is fitted by.

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

With the functions for the dispersion coefficients assuming the form

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

Furthermore A_n and B_n are auxiliary functions and written as

$$A_n = \alpha_0 n^{-\alpha_1}, \quad (9)$$

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

With α_0 , β_0 , α_1 and β_1 are universal dimensionless parameters for all isotropic interactions: $\alpha_0 = 16.36606$, $\beta_0 = 17.19338$, $\alpha_1 = 0.70172$, $\beta_1 = 0.0957$ and $\rho/\alpha_0 = 5.5 + 1.25R_0$, $R_0 = 2(\langle r_A^2 \rangle^{1/2} + \langle r_B^2 \rangle^{1/2})$ are the LeRoy parameter [26]. $\langle r_A^2 \rangle$ and $\langle r_B^2 \rangle$ are the expectation values of squared radii for the outermost electron in atoms A and B, respectively.

3. Results and discussion

3.1 The potential energy function.

The PECs of the NO($X^2\Pi$) electronic state calculated at the CBS limit [CBS/USTE(Q,5)] and the AV6Z theory level, from here we get the data computed employing the AV(Q,5)Z basis sets, are compared in the Figure 1. In Figure 1, the *ab initio* PECs of NO($X^2\Pi$) calculated at AV6Z and the CBS limit using AV(Q,5)Z results. The PECs is aggregated and smooth. Between there PECs well depth than the AV6Z PEC with the difference being ~ 0.001 Eh. In which we take much more exploring time than the AVQZ and AV5Z calculation. The accurate CBS PEC can be obtained with spending less computational, with the extrapolation by using the USTE(Q,5) scheme [29,30].

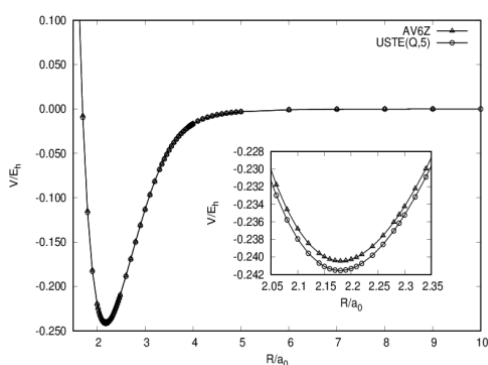


Figure 1: Comparison of the PECs of NO($X^2\Pi$) calculated at AV6Z and extrapolated to the CBS limit using AV(Q,5)Z results.

The EHFACE model [24,25]. is then used least-squares fitting the PECs computed the AVXZ(X=T, Q, 5 and 6) basis sets applied to deduce the APEFs for NO($X^2\Pi$). At AV(Q,5)Z extrapolated to the CBS limit, denoted as CBS/USTE(Q,5). The parameters a_i , D , R_e and γ_i are acquired comply with the least-square fitting process. We try it $n = 3$ to 9 for the total number of coefficients a_i in order to getting a more accurate result. All the parameters of APEFs for NO($X^2\Pi$) are in Table 1 and the *ab initio* and the fitted CBS/USTE(Q,5) PECs are arranged in Fig 2. We can discover, the modeled potential accurately mimics the *ab initio* energies, the error of the maximum just being less than 0.1kcal/mol.

The propose is to estimate the quality of the fitting and we can use the equation below to calculate the root-mean square derivations (ΔE_{RMSD}).

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

Here 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 fitted points ($N=57$). The values of ΔE_{RMSD} are summarized in Table 1. From the Table 1. We can 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 0.01138 kcal/mol, 0.01390 kcal/mol, 0.01747 kcal/mol, 0.01476 kcal/mol, and 0.01708 kcal/mol, respectively. So the quality of this work is really a very accurate fitting.

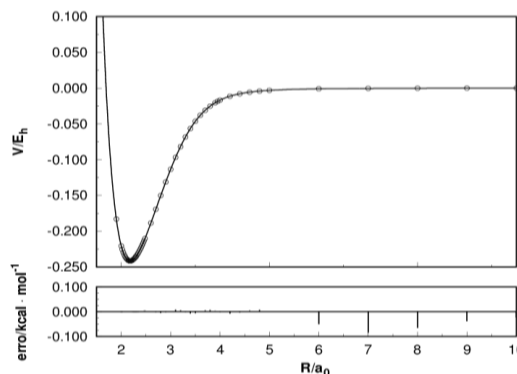


Figure 2: The extrapolated CBS/USTE(Q,5) PECs for NO($X^2\Pi$). The circles indicate the *ab initio* energies, while the line is from the fitted APEF.

3.2 Spectroscopic parameters.

Employing the APEFs achieved by fitting the PECs computed at the MRCI(Q)/AVTZ, MRCI(Q)/AVQZ, MRCI(Q)/AV5Z, MRCI(Q)/AV6Z, and the extrapolated CBS/USTE(Q,5) level, then counting the spectroscopic constants of NO($X^2\Pi$). Among them, K.P.Huber [32] and D.H.Huang [41]. Using CASSCF/6-311G(2d) obtain APEFs. Computing R_e , D_e , B_e , ω_e , $\omega_e \chi_e$ and α_e . Compared the experimental value, the vibrational frequency of them is too large, and by carrying out the MRCI(Q) level of theory calculation with a series of Dunning's basis set. Calculated R_e , ω_e and $\omega_e \chi_e$. The values of D_e , B_e , ω_e , and $\omega_e \chi_e$ are collected in Table 2. and the other theoretical and experimental data [38,41,42,44,46]. For comparison.

$$B_e = \frac{h}{8\pi^2 m R_e^2} \quad (12)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2 m c^2}} \quad (13)$$

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

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

here f_4 is quartic, f_3 is cubic and f_2 is quadratic force parameters, calculated from the APEFs. The values of R_e , ω_e , B_e and $\omega_e \chi_e$ are in Table 2. Presents of R_e , D_e , B_e , ω_e , $\omega_e \chi_e$ and α_e of NO($X^2\Pi$). Comparing with the other theoretical [38,41,42,43,46] and experimental data [45,46]. In this table, it can be concluded that the present results are in good agreement with these results.

We can see that, the well depth (D_e) growth monotonically as the basis set. From AVQZ and the depth D_e is monotonically increasing and the deepest well depth is acquired from CBS/USTE(Q,5) APEFs, due to the difference of 0.0011 E_h from those of the AV6Z APEFs. The equilibrium bond length (R_e) is computed from CBS/USTA(Q,5) APEF to be 2.1795 a_0 , a little bigger than the experimental result 2.1747 a_0 only 0.0048 a_0 , showing high-accuracy. For the vibrational frequency ω_e is computed to be 1897.662 cm^{-1} , comparing with the experiment [44,46] and theoretical [38,41,42,43,46] work the differences are also small. The spectroscopic parameters B_e from CBS/USTE(Q,5) little than the D.H. Huang [41], because of the fact that B_e is inversely proportional to R_e .

The spectroscopic constants between the α_e and $\omega_e \chi_e$ can be affected by α_e and $\omega_e \chi_e$ and the force parameters (quartic f_4 , cubic f_3 and quadratic f_2). The results of α_e and $\omega_e \chi_e$ can be induced to be larger than experiment [44,46] and theoretical work [38,41,42,43,45]. From above work, the present values of the CBS/USTE (Q,5) APEF with the values of AV6Z, the deviations of R_e , D_e , B_e , ω_e , $\omega_e \chi_e$ and α_e are 0.047%, 0.445%, 0.094%, 0.697%, 0.306% and 0.173%, respectively. We can obtain the conclusion that the NO($X^2\Pi$) electronic state spectral parameters in the other theoretical values [38,39,37] and the experimental values [44,46] computed from the CBS/USTE(Q,5) APEF is in good consistent and showing high precision.

Table 1: Fitted parameters of NO($X^2\Pi$) APEFs in Eqs (6) and (7)

Basis sets	AVTZ	AVQZ	AV5Z	AV6Z	CBS(Q,5)
Re/a_0	2.1904	2.1831	2.1811	2.1805	2.1795
D/Eh	0.4215	0.4331	0.4376	0.4409	0.4406
α_1/a_0^{-1}	1.5757	1.9085	2.0643	1.9345	1.6702
α_2/a_0^{-2}	0.3158	0.2001	0.2185	0.1754	0.2077
α_3/a_0^{-3}	3.0609	1.8548	1.3207	1.6537	1.8510
α_4/a_0^{-4}	-1.3688	-0.458	-0.1669	-0.3840	-0.883
α_5/a_0^{-5}	2.6802	0.9606	0.1858	0.7445	1.0667
α_6/a_0^{-6}	-1.1923	-0.669	-0.2266	-0.5718	-0.687
α_7/a_0^{-7}	0.3595	0.2433	0.1097	0.2100	0.2292
γ_0/a_0^{-1}	0.9688	1.3014	1.4593	1.3334	1.0645
γ_1/a_0^{-1}	3.3104	2.6767	3.4174	2.7493	4.3147
γ_2/a_0^{-1}	0.5578	0.3075	0.1543	0.2627	0.2314
$C_6/E_h a_0^{-6}$	31.358	31.952	31.731	31.1093	32.024
$C_8/E_h a_0^{-8}$	509.92	519.59	515.99	505.879	520.76
$C_{10}/E_h a_0^{-10}$	10862.6	11068.47	10991.88	10776.4	11093.3
$\Delta E_{RMSD}/\text{kcal}^* \text{mol}^{-1}$	0.0114	0.0139	0.0175	0.01476	0.0170

3.3 Vibrational manifolds.

By solving the radial Schrödinger equation of the nuclear motion we can obtain the vibrational manifolds, in this work we have to use the program Level 7.5 [36]. By the influence of the adiabatic approximation, theoretical Schrödinger equation can be written as below [37].

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2}{2\mu r^2} J(J+1) + V(r) \phi_{v,J}(r) \quad (16)$$

here $V(r)$ is the rotationless APEF, μ is the molecule reduced mass, and r is the internuclear separation of the two atom, $J(J+1) \hbar^2/2\mu r^2 + V(r)$ is the potential, so $\psi_{v,J}(r)$, $J(r)$ are the eigenfunctions and $E_{v,J}$ are the eigenvalues, J is the rotational quantum numbers and the v is the vibrational quantum numbers. The rotational sublevel can be written by

$$E_{v,J} = G(v) + B_v J(J+1) - D_v J(J+1) - D_v J(J+1)^2 + H_v J(J+1)^3 + L_v J(J+1)^4 + M_v J(J+1)^5 + N_v J(J+1)^6 + O_v J(J+1)^7 \quad (17)$$

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

By solving the Equation (16). We can get the NO($X^2\Pi$)

complete vibrational states when the rotational quantum number $J=0$. Because there are limitations on the length, the first 21 vibrational states can be listed. A complete set of the vibrational states in Table 2. and Table 3. The inertial rotation constants B_v , the vibrational levels $G(v)$ and its classical turning points R_{\max} and R_{\min} and comprise D_v , H_v , L_v , N_v , O_v , and M_v six centrifugal distortion constants can be obtained. Computed from both the AV6Z and CBS/USTE(Q,5) APEFs for NO($X^2\Pi$). Table 3. list the classical turning points, the vibrational levels $G(v)$, and the inertial rotation constants B_v . And from that table we also can see that the CBS/USTE(Q,5).

APEF produces a little larger vibrational levels $G(v)$ than AV6Z APEF, are only by 0.668 cm^{-1} (0.071%) and 49.587 cm^{-1} (0.150%) for $v=0$ and 20, respectively. Obviously the deviation becomes more as the number of vibrations v increases. With the biggest difference can be found to 36.978 cm^{-1} when $v=20$. The value of $2.7843 \times 10^{-3} \text{cm}^{-1}$, $1.2 \times 10^{-3} \text{cm}^{-1} a_0$ and $2.66 \times 10^{-3} \text{cm}^{-1} a_0$, respectively. The inertial rotation constants B_v is the largest different is at $v=20$. The inertial rotation constants and classical turning points difference at 10^{-3} magnitude, showing a high quality with each other.

The six centrifugal distortion constants H_v , N_v , L_v , D_v ,

O_v and M_v in Table 4 and Table 5 present obtained from the AV6Z and CBS/USTE(Q,5) APEFs, the deviation of the six centrifugal distortion constants are small. As far as we know, Theory data and experiment results have not been acquired in other literature on the vibrational levels, inertial rotation constants, centrifugal distortion constants and classical turning points. Therefore, between them we cannot compare directly, but according to these APEFs the high precision

fittings. The good agreement between the spectroscopic parameters and the results in the literature [38,41,44,46]. So we can believe that the results listed in Tables 3, 4, 5 are precise and credible. Moreover, the less costly of CBS/USTE(Q,5) scheme, we can acquire the APEF from above lists which can give us results as good as those at the interaction potential energy of NO(X²Π) well.

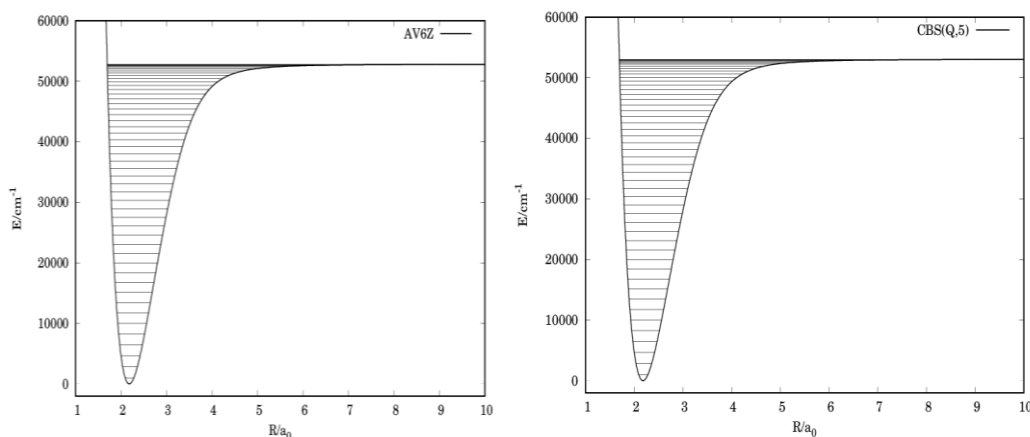


Figure 3: A comparison of the vibrational energy spectrum for NO(X²Π). Left panel: the vibrational energy spectrum obtained from the extrapolated AV6Z. Right panel: the vibrational energy spectrum obtained from the extrapolated CBS/USTE(Q,5).

Table 2: Spectroscopic constants compared with experimental and other theoretical data for the NO(X²Π) 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	0.230681	2.190421	1871.269	1.680399	0.019989	17.291
AVQZ	0.237602	2.183101	1889.941	1.691685	0.019820	17.124
AV5Z	0.239592	2.181076	1896.666	1.694829	0.019778	17.103
AV6Z	0.240459	2.180514	1896.339	1.695702	0.019738	17.035
CBS(Q,5)	0.241535	2.179493	1897.662	1.697291	0.019704	16.983
Theory		2.1817	1885.0	1.693	0.0170	12.89
Theory[38]		0.11508	1904.03			
Theory[41]		0.1160	1988.412	1.7301	0.0148	16.466
Theory[42]		0.1161	1878.0	1.6753	0.0182	16.252
Theory[43]		0.121	1913			25
Theory[45]		1.1507	1906.6			
Expt	–	2.1747	1904.0	1.720	0.0182	14.10
Expt[46]		1.1508	1904.03	1.7046	0.0178	13.97

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 NO(X2 Π) when $J = 0$, predicted by the CBS/USTE(Q,5) and AV6Z APEFs.

v	BCBS/USTE(Q, 5)				AV6Z			
	G (v)	R_{\min}	R_{\max}	B_v	G (v)	R_{\min}	R_{\max}	B_v
0	945.475	2.09270	2.27764	1.688674	944.807	2.09369	2.27869	1.6871046
1	2815.539	2.03551	2.35778	1.671304	2813.339	2.03645	2.35887	1.6697587
2	4657.961	1.99896	2.41762	1.6538821	4654.027	1.99989	2.41874	1.652339
3	6472.741	1.97086	2.46935	1.6364105	6466.898	1.97177	2.47053	1.6348560
4	8259.888	1.94767	2.51653	1.6188921	8251.989	1.94857	2.51776	1.6173134
5	10019.420	1.92778	2.56077	1.6013282	10009.346	1.92868	2.56205	1.5997167
6	11751.359	1.91031	2.60297	1.5837190	11739.016	1.91120	2.60430	1.5820681
7	13455.724	1.89469	2.64369	1.5660626	13441.041	1.89559	2.64509	1.5643676
8	15132.526	1.88056	2.68332	1.5483552	15115.452	1.88147	2.68478	1.54661233
9	16781.764	1.86765	2.72214	1.5305905	16762.261	1.86857	2.72367	1.5287962
10	18403.416	1.85577	2.76037	1.5127596	18381.456	1.85670	2.76196	1.5109101
11	19997.435	1.84476	2.79817	1.4948502	19972.992	1.84572	2.79983	1.4929415
12	21563.741	1.83453	2.83568	1.4768470	21536.790	1.83550	2.83742	1.4748741
13	23102.216	1.82496	2.87302	1.4587312	23072.723	1.82596	2.87484	1.4566881
14	24612.696	1.81599	2.91031	1.4404800	24580.618	1.81701	2.91221	1.4383598
15	26094.967	1.80755	2.94764	1.4220668	26060.244	1.80860	2.94964	1.4198613
16	27548.757	1.79960	2.98511	1.4034608	27511.309	1.80067	2.98721	1.40116100
17	28973.730	1.79209	3.02282	1.3846267	28933.458	1.79319	3.02504	1.3822224
18	30369.480	1.78498	3.06086	1.3655244	30326.260	1.78612	3.06321	1.36300504
19	31735.526	1.77825	3.09934	1.3461089	31689.210	1.77941	3.10184	1.3434629
20	33071.306	1.77186	3.13836	1.3263291	33021.719	1.77306	3.14102	1.3235448

Table 4: Centrifugal distortion constants (in cm^{-1}) of the first 21 vibrational states for NO(X2 Π) when $J = 0$, calculated from CBS/USTE(Q,5) APEF.

v	$D_v/10^{-6}$	$H_v/10^{-12}$	$L_v/10^{-17}$	$M_v/10^{-22}$	$N_v/10^{-27}$	$O_v/10^{-32}$
0	5.437992	1.559502	-4.166894	-2.425039	-2.150027	-1.448431
1	5.451838	1.239135	-4.375710	-2.433793	-2.343937	-1.995619
2	5.4666462	0.9302671	-4.589691	-2.534883	-2.714808	-2.613328
3	5.482337	0.6272560	-4.827772	-2.760155	-3.325046	-3.432708
4	5.498906	0.3224950	-5.112399	-3.147544	-4.216222	-4.243475
5	5.516433	0.0064120	-5.468469	-3.736607	-5.441234	-4.890768
6	5.535086	-0.332562	-5.923436	-4.569518	-7.034359	-4.671716
7	5.555130	-0.707892	-6.506343	-5.686767	-9.085523	-4.392779
8	5.576932	-1.134936	-7.249254	-7.142433	-11.63127	-1.717421
9	5.600959	-1.630845	-8.186195	-8.995197	-14.74421	6.071908
10	5.627789	-2.214518	-9.352743	-11.29770	-18.61874	15.87140
11	5.658101	-2.906711	-10.79022	-14.14308	-23.38521	33.64130
12	5.692686	-3.730146	-12.54483	-17.64192	-29.26966	65.23391
13	5.732446	-4.709845	-14.67073	-21.93796	-36.63015	116.5468
14	5.778400	-5.873521	-17.23012	-27.18302	-46.33422	166.8755
15	5.831690	-7.252815	-20.30628	-33.64659	-58.49475	250.4761
16	5.893589	8.883492	-24.00188	-41.71612	-74.33507	388.2012
17	5.965531	-10.80752	-28.44377	-51.79540	-95.40294	563.7147
18	6.049123	-13.07461	-33.79720	-64.47615	-123.7367	776.4947
19	6.146177	-15.74437	-40.28211	-80.67976	-162.5084	1064.715
20	6.258795	-18.88581	-48.04638	-99.49040	-234.2097	-594.8964

4. Conclusions

The PECs of NO(X2II) molecule have been calculated by fitting *ab initio* energies computed employing the CASSCF wave function as a reference, followed by the MRCI(Q) approach with a series of correlation-consistent AVXZ(X=T,Q,5,6) basis sets. The USTE(Q,5) scheme is employed to extrapolate the PECs to the CBS limit by computed with aug-cc-pV(Q,5)Z basis sets. Subsequently the PECs are fitted to APEFs by using the EHFACE model. Based on the NO(X2II) APEFs. Calculating the spectroscopic information, D_e , R_e , ω_e , B_e , α_e and $\omega_e x_e$. By Comparison with the effective experiment results, the computational data obtained from the CBS/USTE(Q,5) and AV6Z APEF expressing high precision. So they can be used to perform the calculations of vibrational manifolds. Then, by solving the radial Schrödinger equation of nuclear motion employing the Numerov approach, the complete set of

vibrational states has been calculated at the first time. For each vibrational state, one vibrational level and its classical turning points: one inertial rotation constant, six centrifugal distortion constants and also obtained. As a whole, in the present study our results show a more precise investigations of the vibrational manifolds and spectroscopic constants of the NO(X2II) molecule.

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Table 5: Centrifugal distortion constants (in cm^{-1}) of the first 21 vibrational states for NO(X2II) when $J = 0$, calculated from AV6Z APEF.

v	$D_v/10^{-6}$	$H_v/10^{-12}$	$L_v/10^{-17}$	$M_v/10^{-22}$	$N_v/10^{-27}$	$O_v/10^{-32}$
0	5.431783	1.576946	-4.399691	-2.828356	-1.597696	-1.313618
1	5.448217	1.197313	-4.420951	-2.794155	-1.911876	-1.953018
2	5.464728	0.8394907	-4.471887	-2.879827	-2.425023	-2.743647
3	5.481326	0.4946226	-4.573355	-3.119913	-3.191733	-3.665915
4	5.498109	0.1519854	-4.748878	-3.550359	-4.251985	-4.597927
5	5.515265	-0.200911	-5.023748	-4.206712	-5.648099	-5.488699
6	5.533083	-0.578217	-5.425110	-5.129773	-7.400288	-5.022209
7	5.551949	-0.995571	-5.980131	-6.349690	-9.593762	-4.584563
8	5.572347	-1.470000	-6.718463	-7.915712	-12.25622	-1.419169
9	5.594860	-2.019791	-7.670914	-9.880432	-15.46727	6.977009
10	5.620169	-2.664459	-8.869391	-12.29179	-19.42491	17.55813
11	5.649049	-3.424887	-10.35164	-15.24166	-24.27441	36.34036
12	5.682369	-4.323527	-12.16062	-18.84168	-30.26223	69.12569
13	5.721093	-5.384828	-14.34788	-23.23939	-37.77534	121.4542
14	5.766290	-6.635742	-16.97388	-28.59181	-47.72780	171.1074
15	5.819136	-8.107095	-20.12154	-35.17907	-60.25653	252.3245
16	5.880925	-9.833875	-23.89438	-43.40227	-76.65808	384.0754
17	5.953100	-11.85744	-28.42150	-53.67969	-98.55727	546.8707
18	6.037269	-14.22714	-33.87208	-66.62043	-128.1653	730.3626
19	6.135236	-17.00300	-40.48267	-83.32861	-167.1936	1125.535
20	6.249099	-20.25341	-48.38369	-102.6131	-242.0836	-620.4310

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