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Accurate *ab initio*-based potential energy curve and spectroscopic properties of NO(X²Π) via extrapolation to the complete basis set limit

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Abstract. The potential energy curves (PECs) of NO (X²Π) 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 $A^2\sum^+ - \chi^2\pi$ and $D^2\sum^+ - \chi^2\pi$ 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: $A^2\sum^+ - \chi^2\Pi$ (γ system) and $B^2\Pi - \chi^2\Pi$ (β system) $B^2\prod$, 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 $A^2\sum^+$ state, it is the longest wavelength of NO absorption system [10]. Studying on the accurate APEF of NO(X²Π) 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(X²Π).

In the present work, we counted the PECs of the NO(X²Π) 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(X²Π), 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(X²Π). 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 section2, 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].

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

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

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

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

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.

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

As is written as the auxiliary relation

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

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 (X2Π).

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

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

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

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

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, $a_i(i=1,\ldots,n)$ 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.

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

With the functions for the dispersion coefficients assuming the form

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

Furthermore A_n and B_n are auxiliary functions and written as