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Calculation of Spectroscopic Constants and Vibrational Levels in the $X^2\Pi$, $a^4\Pi$, and $B^2\Pi$ States of Nitric Oxide*

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Abstract: The equilibrium structure and single-point energy scanning of the ground state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ of NO molecule are calculated using the CASSCF/MRCI method and the cc-pVDZ basis set. The potential energy curves are obtained by a least square fitting to the modified Murrell-Sorbie function. Employing the Rydberg-Klein-Rees method, the harmonic frequency and other spectroscopic data ($\alpha_e, \omega_e, \omega_e\chi_e, \beta_e$) of the ground state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ of NO molecule are calculated and the calculation results are in better agreement with the experimental ones than other theoretical data. In addition, the eigenvalues of vibrational levels are calculated by solving the radial one-dimensional Schrödinger equation based on the analytical potential energy function.

Key words: Potential energy function; Multireference configuration interaction; Harmonic frequency; Vibrational levels

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0 Introduction

Nitric oxide (NO) plays a significant role in a wide range of chemical and physical processes which include its contribution to photochemical smog, and its well known role in atmospheric phenomena including dayglow and auroral processes. The accurate knowledge for the altitude dependence of NO concentration is essential for the understanding of atmospheric chemistry^[1]. NO is an open shell molecule, and the valence electronic configuration is given by $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (4\sigma)^2 (5\sigma)^2 (1\pi)^4 (1\pi)^1$ ^[2]. Studies of the electronic structure and spectroscopic data of the NO molecule have been increasing interests to the chemical or physical scientists. This is due to the progress of the instruments used in satellites and rockets, which has made it possible to determine the composition of the outer atmosphere^[3]. The ground state of nitric oxide, NO ($X^2\Pi$), is an important emitter in the atmosphere. Radiation from its fundamental ($5.4 \mu\text{m}$) and first overtone ($207 \mu\text{m}$) rotation-vibration transitions have been observed in atmospheric emission spectra under both disturbed (auroral) and ambient conditions^[4]. The NO ($a^4\Pi$) state is the lowest

electronically excited state of the NO molecule, and is metastable with respect to optical transitions to the ground state^[5]. The $B^2\Pi$ of NO is a valence-type state and the $C^2\Pi$ Rydberg-type state. An obvious character of the Rydberg states is the strong photoelectron spectra from the $\Delta v = 0$ transition^[6]. F. Grein and A. Kapur reported that the $C^2\Pi$ Rydberg state joins with the $B^2\Pi$ valence state at approximately 0.116 nm ^[7]. The analysis of the absorption spectrum of NO have revealed a wealth of detailed information concerning the mutual perturbation between the bands of the β ($B^2\Pi-X^2\Pi$) and δ ($C^2\Pi-X^2\Pi$) systems. R. Gallusser and K. Dressler have presented information on the higher electronic states of the $n\pi$ Rydberg series $3p C^2\Pi$, $4p K^2\Pi$, $5p Q^2\Pi$, $6p W^2\Pi$ and on the second excited $^2\Pi$ state of valence character $L^2\Pi$ ^[8]. High quantum states belonging to the A-X (0-1) band of NO have been found to be the most valuable and have led to a NO mole fraction determination with an accuracy of $\pm 13\%$. NO absorption in the flame was completely masked using the A-X (0-0) band^[9]. Electronic quenching of NO ($A^2\Sigma^+$) is also important for understanding the intermolecular properties related to the collision complex formation^[10]. Ref. [11] has calculated the PES for several configurations of the NO - Ne dimer, using highly accurate ab initio quantum chemistry techniques and fitted them to a simple analytical form convenient for further dynamical studies. The accurate potential energy

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surface available for NO + Ar systems were calculated by using CCSD(T) method^[12]. The $C^2\Pi$, $A^2\Pi$, $B^2\Pi$, and $b^4\Sigma^-$ states are all formed, directly or indirectly, from the $a^2\Pi$ state^[13]. The NO γ system ($A^2\Sigma^+ - X^2\Pi$) has been used to measure NO column densities in the mesosphere and for the interpretation of emissions in aurora^[14]. Ref. [15] reported the magnetic hyperfine parameters of NO($X^2\Pi$). Predictions of the spectroscopic constants of diatomic molecules, e. g. , ω_e , $\omega_e\chi_e$, β_e and α_e are often used to benchmark new theoretical methods or study electron correlation or basis set effects. Based on the theory of atomic and molecular statics, the reasonable dissociation limit for the ground state ($X^2\Pi$) and the excited $a^2\Pi$ and $B^2\Pi$ of NO molecule are derived. Using the CASSCF/MRCI approach, the equilibrium geometry of the ground state ($X^2\Pi$) and the excited states $a^2\Pi$ and $B^2\Pi$ of NO molecule are calculated. At the same time, the single point energy scanning calculation is also made at cc-pVDZ basis set near the equilibrium inter-nuclear separation obtained by the geometry optimization so as to attain the more accurate result. A least square fitting to the Murrell-Sorbie function is made and other spectroscopic data (α_e , ω_e , $\omega_e\chi_e$, β_e) are further computed, which are in good agreement with the experimental results. In addition, with the analytic potential energy function obtained on the CASSCF/MRCI level, we have also calculated the vibrational levels by solving the radial Schrödinger equation of nuclear motion.

1 Computational details

1.1 Determination of appropriate dissociation limit

The interaction of atoms within a molecule is governed by the electronic potential energy surface of the system. It describes the molecular structure and molecular spectrum and founds the base of researching the time-dependant process, which matches a definite electronic state of a molecule or radical^[16-17]. Potentials can be calculated using ab initio calculation, by choosing a set of internuclear separations, solving the resulting Schrödinger equation for the electronic motion and repeating the procedure until a grid of points has been generated. In order to describe the systematic potential function accurately, the proper dissociation limit of NO radical and conceivable electronic configuration must be determined.

Nitric oxide is an open shell molecule and the

electronic configuration of the ground state of NO ($X^2\Pi$) is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi_x^2 1\pi_y^2 2\pi_x^1$ which has A' symmetry^[7]. The outermost electron occupies an antibonding orbital, namely $2\pi_x^1$. The $a^4\Pi$ state of NO is the lowest excited states and have three reference configurations which are $1\pi_y \rightarrow 2\pi_y$, $1\pi_x \rightarrow 3\pi_x$, $1\pi_x 1\pi_y \rightarrow 2\pi_x 2\pi_y$. The dominant configuration is $1\pi_y \rightarrow 2\pi_y$. The dominant configurations corresponding to the $B^2\Pi$ states are $1\pi_x \rightarrow 2\pi_x$ and $1\pi_y \rightarrow 2\pi_y$.

According to the atomic and molecular reaction statics^[16-17], the possible electronic states can be determined. The ground electronic state of O atom is 3P_g , and that of N atom is 4S_u , which belongs to the $SU(n)$ group. NO radical is in $C_{\infty v}$ group. When the N(4S_u) atom reacts with O(3P_g) atom and produces NO molecule, the systematic symmetry decreased. The irreducible representation of $SU(n)$ group can be decomposed into the direct sum of the irreducible representation of $C_{\infty v}$ group. Using direct product and reduction, the irreducible representation of $C_{\infty v}$ group can be obtained, namely the possible electronic states can be determined. The direct sum of irreducible representation of C(3P_g) and O(3P_g) resolution into $C_{\infty v}$ group are

$$^3P_g \rightarrow ^3\Sigma \oplus ^3\Pi \quad (1)$$

$$^4S_u \rightarrow ^4\Sigma^- \quad (2)$$

The ground state electronic configuration of N atom is 4S_u . The irreducible representation of N(4S_u) decomposition into $C_{\infty v}$ group is $^4\Sigma_u^-$. On the direct sum and reduction to the combination of NO($^3P_g + ^4S_u$), it should be determined that the combination of ($^3\Sigma \oplus \Pi$) \oplus ($^4\Sigma^-$) includes the ground state ($X^2\Pi$) of NO molecule. So the combination of the ground state O and N atom can produce the the ground state ($X^2\Pi$) of NO molecule. According to the invertible principle of micro-process^[17], the dissociation limit of the ground state ($X^2\Pi$) and excited states ($a^4\Pi$, and $B^2\Pi$) of NO molecule respectively are

$$NO(X^2\Pi) \rightarrow O(^3P_g) + N(^4S_u) \quad (3)$$

$$NO(a^4\Pi) \rightarrow O(^3P_g) + N(^4S_u) \quad (4)$$

$$NO(B^2\Pi) \rightarrow O(^1D) + N(^4S_u) \quad (5)$$

1.2 Computational methods

The multireference configuration interaction (MRCI) is employed in the calculations, which offered an efficient and uniform way of treating multi-configurations effects in the whole region of inter atomic separations for the ground and excited electronic states. A full CI exactly solves the

Schrödinger equation within some basis sets, but is usually too complex a calculation to compute molecules containing more electrons. The single reference methods can almost always be done, and usually are not very challenging (to the computer or the user), however, their accuracy is limited. MRCI is a way to systematically include those CSFs that contribute most significantly to the correlation energy^[18]. The orbitals for the CI calculations of NO molecule are derived from a multi-configuration self-consistent field (MC-SCF) solution, obtained in complete active space self-consistent field (CASSCF) method. The full valence active space consists of eight valence orbitals 3 σ -6 σ , 1 π , 2 π , which denoted by (422) in C_{2v} point group symmetry. Within each spin symmetry, a common set of averaged natural orbitals to be used for all states was computed using the CASSCF (11, 8) wavefunctions, where all possible electronic excitations resulting from the distribution of 11 electrons into 8 active orbitals (4, 2, 2, 0) \equiv (4 $\times a_1$, 2 $\times b_1$, 2 $\times b_2$, 0 $\times a_2$) were allowed. The incorporation of as much dynamic correlation as possible in the final wavefunction was made with a multireference configuration interaction wavefunction (MRCI), with the inclusion of all single and double excitations from the reference sets generated by all CASSCF configurations. In all calculations core orbitals were kept frozen.

Although there are many basis sets that we can choose, only few ones work well. The atomic basis functions used in the present investigation is the correlation-consistent polarized valence quadruple-zeta (cc-pVDZ) type developed by Dunning and co-workers as obtained from the latest version available at the extensible computational chemistry environment basis set database^[18]. The correlation-consistent polarized valence doublezeta basis set, cc-pVDZ, is formed from a contraction of (9s4p1d) to [3s2p1d], and is augmented by a diffuse set of functions (1s1p1d), resulting in a contraction scheme of (10s5p2d)/[4s3p2d]. The diffuse functions are included primarily to facilitate comparison to forthcoming studies of excited electronic states.

The single point energy of the ground state the ground state ($X^2\Pi$) and the excited states ($a^4\Pi$ and $B^2\Pi$) of NO radical are scanned using CASSCF/MRCI approach, and then the series of single point energy are obtained. During single point energy scanning, all of the parameters except

the inter-nuclear distance R between two atoms N and O are kept consistent with that used in the calculation of optimization of molecular structure. The calculations at CASSCF/MRCI level are started with the internuclear distance of 0.36 nm, and the internal is 0.004 nm. Totally, 69, 65 and 69 points were calculated respectively for the ground state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ of NO molecule. Parts of the single point energies for different states are listed in the Table 1 which is the base of our further calculations.

Table 1 The potential energies $E(R)$ at different inter-nuclear distance of the $X^2\Pi$, $a^4\Pi$ and $B^2\Pi$ states of NO molecule

R/nm	$E(R)/\text{Hartree}$		
	$X^2\Pi$	$a^4\Pi$	$B^2\Pi$
0.100	129.444 2	129.062 4	
0.104	129.476 5	129.1293	128.840 8
0.112	129.504 8	129.220 2	129.160 3
0.124	129.495	129.288 7	129.308 9
0.140	129.443 9	129.313 8	129.345 3
0.156	129.388 6	129.305 2	129.340 6
0.172	129.344 3	129.284 7	129.326 8
0.188	129.313 4	129.262 5	129.310 0
0.208	129.290 2	129.238 9	129.289 0
0.232	129.276 5	129.219 1	129.275 1
0.256	129.270 8	129.207 4	129.270 4
0.280	129.268 5	129.201 0	129.268 2
0.304	129.267 7	129.197 7	129.267 3
0.328	129.267 4	129.196 1	129.267
0.352	129.267 3	129.195 3	129.266 8

2 Results and discussion

2.1 Analytical potential energy function and spectroscopic parameters

Among the functions that proposed to fit analytical potential energy functions (APEFs) of diatomic molecules, Murrel - Sorbie (MS) potential energy function seems to be the best. It can accurately reproduce interaction molecules, and has been used to deduce APEFs for many molecules. So the series of single point energy are fitted as the following Murrel-Sorbie functions (6) using the normal equations.

$$V(\rho) = -De(1 + \alpha_1\rho + \alpha_2\rho^2 + \alpha_3\rho^3)\exp(-\alpha_1\rho) \quad (6)$$
Where ρ equals $r - r_e$, r is the inter-nuclear distance and r_e is Equilibrium inter-nuclear distance of N and O atom. De is the dissociation energy and α_1 , α_2 and α_3 are fitting coefficient. The parameters α_1 , α_2 and α_3 and De are determined by fitting. It is significant to point out that r_e is also treated as a fitting parameter during the fitting process. In

many cases satisfactory results can be obtained when n equals 3^[16-17], so we use the MS function as formula (6).

The potential energy curves of the ground state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ of NO molecule showed in the Fig. 1 with the minimum energy points demonstrate that the ground state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ of NO molecule can exist stably. By iterating a system of normal equations based on a least-square fit, the parameters α_1 , α_2 and α_3 of Eq. (6) have been calculated for the ground state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ of NO molecule and tabulated in Table 2 together with the dissociation energies and equilibrium inter-nuclear separations for convenient comparison. We have made simple comparison between the experimental and other theoretical values^[4, 13, 16]. In Fig. 1, three the potential energy curves stand for the different states $X^2\Pi$, $a^4\Pi$ and $B^2\Pi$ of NO molecule respectively. Considering the equilibrium positions (r_e), the dissociation limit and dissociation energy (De) of the system, we can conclude that three curves would provide us with relatively reasonable results, and are worthy of further investigation. Either the equilibrium positions or the dissociation energies of the curves of different states of NO are satisfactory and are in good agreement with the experimental ones. These three curves are used to fit to the Murrell-Sorbie potential functions and because they also provide us with good results. The least square fitting is a widely used method in fitting work, and in our fitting process, it is carried out with Levenberg-Marquardt method employing Matlab program. The fitting parameters of analytical potential energy functions are tabulated in Table 2 while other theoretical and experimental counterparts are also collected.

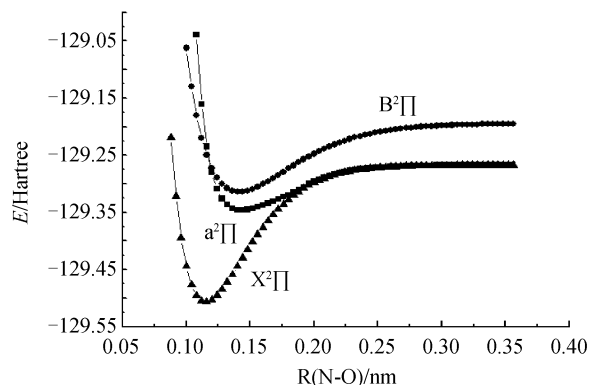


Fig. 1 The potential energy curves of the ground state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ of NO. From the Table 2, we can easily see that the

computed dissociation energy is in agreement with the experimental value^[16] within -0.096 eV deviation for the $X^2\Pi$ state, and the r_e is 0.11502 nm with 0.0006 nm deviation. Deviations 0.00122 of r_e from Ref. [19] are larger than ours. The De of the excited state $a^4\Pi$ and $B^2\Pi$ are also in accordance with the experimental counterparts^[8] within 0.007 eV and 0.004 eV respectively, and the computed equilibrium inter-nuclear distance of $a^4\Pi$ and $B^2\Pi$ states are in accord with the experimental data^[8] within 0.0002 nm error or 0.14% for the $a^4\Pi$ state, and 0.0007 nm error or 0.48% for the $B^2\Pi$ state at the present at CASSCF/MRCI calculation level of theory in full active space, respectively. Comparison of the theoretical determinations of the dissociation energies and the equilibrium inter-nuclear distances with the previous other theoretical results^[2, 8, 19, 28-29] clearly shows that the present work represents an improvement in agreement with experiments.

Table 2 The constants for the ground state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ states of NO molecule

States	T_e /eV	r_e /nm	De /eV	Data source
$X^2\Pi$	0.00	0.11502	6.518	This work
	0.00	0.11530	5.850	Ref. [8]
	0.00	0.11508	6.614	Ref. [16]
	0.00	0.11499	6.471	Ref. [2]
	0.00	0.11630	6.260	Ref. [19]
$a^4\Pi$	4.39	0.1438	1.467	This work
	4.39	0.1400	1.460	Ref. [28]
	4.77	0.1436	1.90	Ref. [8]
$B^2\Pi$	5.71	0.1420	3.203	This work
	5.25	0.1427	3.190	Ref. [8]
	5.69	0.1417	3.30	Ref. [29]

It is known to us all that the properties round the equilibrium position are what we really care, so we just employed 69, 65 and 69 energy points respectively for the ground state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ at different inter-nuclear distance of N and O atoms. The r_e obtained using molecule structure optimization method is accordance with the one obtained with the single point scanning method. So we can conclude that the present calculation approach is reliable.

2.2 Calculation of harmonic frequency of NO radical

Force constant of second order can be derived from analytical potential energy equation (6).

$$f_2 = De(a_1^2 - 2a_2) \quad (7)$$

On the other hand, diatomic molecule force

constant of second order is related with the harmonic frequency as following equation according to the RKR method^[16].

$$f_2 = 4\pi^2 \omega_e^2 \mu c^2 \quad (8)$$

Eq. (9) can be derived from equation (7) and (8).

$$\omega_e = \left[\frac{D_e(a_1^2 - 2a_2)}{4\pi^2 \mu c^2} \right]^{1/2} \quad (9)$$

Where μ is the diatomic molecule reduced mass, and c is the speed of light in vacuum. The other spectroscopic constants can be calculated from following equations.

$$f_3 = -6D_e \left[a_3 - a_1 a_2 - \frac{1}{3} a_1^3 \right] \quad (10)$$

$$f_4 = D_e (3a_1^4 - 12a_1^2 a_2 + 24a_1 a_3) \quad (11)$$

Where f_2 , f_3 and f_4 are quadratic, cubic and quartic force constants respectively, after calculation of force constants and harmonic frequency, other spectroscopic constants can be computed using following equations.

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

$$a_e = -\frac{6B_e^2}{\omega_e} \left[1 + \frac{f_3 R_e}{3f_2} \right] \quad (13)$$

$$\omega_e \chi_e = \frac{B_e}{8} \left[-\frac{f_4 R_e^2}{f_2} + 15 \left(1 + \frac{\omega_e a_e}{6B_e^2} \right)^2 \right] \quad (14)$$

The calculation results of spectroscopic constants are tabulated in the Table 3 and 4.

Table 3 The force constants for the ground state X²Π and the excited states a⁴Π and B²Π states of NO molecule

States	$f_2/(\text{eV} \cdot \text{nm}^{-2})$	$f_3/(\text{eV} \cdot \text{nm}^{-3})$	$f_4/(\text{eV} \cdot \text{nm}^{-4})$
X ² Π	1.002 4e+3	-7.612 1e+5	4.696 0e+7
a ⁴ Π	2.60 3e+3	-2.216 9e+5	1.988 8e+7
B ² Π	2.97 2e+3	-1.724 2e+5	8.100 7e+6

Table 4 The spectroscopic constants for NO molecule

States	ω_e/cm^{-1}	$\omega_e \chi_e/\text{cm}^{-1}$	B_e/cm^{-1}	a_e/cm^{-1}	Data source
X ² Π	1 909. 4	14. 86	1. 69	0. 020	This work
	1904. 2	14. 08	1. 67	0. 017	Ref. [8]
	1 915. 0	14. 65	1. 71	0. 017 4	Ref. [19]
	2 014. 8	26. 34	1. 67	0. 020	Ref. [20]
a ⁴ Π	986. 6	12. 6	1. 13	0. 021	This work
	1 017. 0	10. 69	1. 12	0. 017	Ref. [20]
	970. 8	12. 6	1. 10	0. 023	Ref. [8]
	756	16. 0	--	--	Ref. [19]
B ² Π	1 028. 6	9. 8	1. 12	0. 013	this work
	1 154. 0	14. 0	1. 00	0. 014	Ref. [20]
	1 221. 0	56. 4	1. 11	0. 015	Ref. [8]
	1 037. 2	7. 7	1. 092	0. 012	Ref. [19]

From table 4, the harmonic frequency (ω_e) obtained by this work for the ground state X²Π is 1 909. 4 and much closer to the experimental data^[19] than the data of Ref. [8, 20]. In detail the anharmonic frequency ($\omega_e \chi_e$) we present for B²Π

state is more accurate to the experimental data^[19] than ones of Ref. [8, 20]. By comparing the harmonic frequency and other spectroscopic data between theory and experimental values we find that our method has an obvious improvement in accuracy.

2.3 Calculation of vibrational levels of NO radical based on the analytical potential energy functions

Vibrational spectroscopy has a fundamental role in molecular physics and its applications extend to other fields like astronomy, biology and earth and environmental sciences. Vibrational molecular analysis provides important information on the structure of the molecules^[22]. The RKR method^[16] has become standard procedure for the calculation of potential curves for diatomic molecules. In previous calculations, the initial input set of constants for the ground state X²Π and the excited states a⁴Π and B²Π states of NO was established by spectra for $v \leq 8$, a range covering vibrational levels only in the lower half of each potential well. We provided a useful way to obtain the spectroscopic constants used as input of the RKR calculations based on the analytical potential energy function and a series of eigenvalues of vibrational levels is determined. These levels lie close to the dissociation limit, furnishing better spectroscopic constants for constructing the RKR curves of the ground state X²Π and the excited states a⁴Π and B²Π states of NO.

Table 5 Eigenvalues of vibrational levels (E_v in cm⁻¹) for the ground state X²Π and the excited states a⁴Π and B²Π states of NO molecule

States	v	E_v/cm^{-1}	Ref. [21]	v	E_v/cm^{-1}	
X ² Π	0	959. 6	959. 6	11	20 040. 2	
	2	4 672. 7	4627. 3	14	24 657. 4	
	4	8 316. 5	8 283. 5	17	29 036. 6	
	6	11 803. 3	11 782. 3	19	31 856. 5	
	8	15 170. 6		23	37 552. 1	
	a ⁴ Π	0	482. 2		11	9 497. 0
3		3 243. 3		14	11 426. 5	
5		4 958. 1		16	12 589. 4	
7		6 571. 9		18	13 659. 8	
9		8 084. 9		21	15 124. 9	
B ² Π		0	527. 9		11	10912. 5
		3	3 598. 4		14	14 232. 7
	5	5 502. 1		16	15 800. 9	
	7	7 346. 9		18	17 297. 5	
	9	9 163. 5		21	19 438. 9	

The vibrational energy levels (E_v in cm⁻¹) are obtained by solving the radial one-dimensional Schrödinger equation of nuclear motion.

$$\left[-\frac{\hbar^2 d^2}{2\mu dr^2} + \frac{\hbar^2}{2\mu r^2} J(J+1) + V(r)\right] \Psi_{v,J}(r) = E_{v,J} \Psi_{v,J}(r) \quad (15)$$

Where $V(r)$ denotes analytical potential energy function. The v and J denote vibrational quantum number and rotational quantum number respectively. When J equals to 0, E_v is eigenvalue of vibrational energy. The eigenvalues of vibrational levels are compared with that of literature^[21].

3 Summary

The equilibrium structure of the ground state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ states of NO molecule are calculated using the CASSCF/MRCI method and the cc-pVDZ basis set, and analytical potential energy functions are fitted. On the basis of physical theory of potential energy functions, harmonic frequency and other spectroscopic constants are calculated employing the Rydberg-Klein-Rees method. The theoretical calculation results are in excellent agreement with the experiments and are more accurate than the other theoretical ones, which mean that calculation method presented in this paper is reliable and feasible. In addition the eigenvalues of vibrational levels of state $X^2\Pi$ and the excited states $a^4\Pi$ and $B^2\Pi$ states of NO molecule are derived by solving the one-dimensional Schrödinger equation of nuclear motion.

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NO 分子的基态($X^2\Pi$)和激发态($a^4\Pi$ and $B^2\Pi$) 光谱常量和振动能级的计算

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摘要: 本文使用完全活性空间自洽场/多组态相互作用 (CAS SCF/MRCI) 理论, 以 cc-pVDZ 为基组, 计算了 NO 分子基态($X^2\Pi$)和激发态 ($a^4\Pi$ and $B^2\Pi$)的平衡结构和单点能扫描曲线. 采用最小二乘法拟合了 Murrell-Sorbie 函数, 得到了 NO 分子的解析势能曲线, 并利用 Rydberg-Klein-Rees 方法, 计算得到的 NO 分子相应态的谐振频率和其它的光谱数据(ω_e , α_e , $\omega_e\chi_e$, β_e)与实验值十分一致, 和其它理论计算方法进行比较, 发现该方法有更好的准确性. 以得到的解析势能函数为基础, 求解 NO 分子核运动的一维径向 Schrödinger 方程, 获得了更高振动态的振动能级.

关键词: 势能函数; 多组态相互作用; 谐振频率; 振动能级



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