

# Electronic Structure with Rovibrational and Dipole Moment Study of the NiO Molecule

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Received June 10, 2012; revised July 9, 2012; accepted July 31, 2012

## ABSTRACT

The potential energy curves have been investigated for the 40 lowest electronic states in the  $2s+1\Lambda^{(\pm)}$  representation below  $25,000\text{ cm}^{-1}$  of the molecule NiO via CASSCF, MRCI (single and double excitation with Davidson correction) and CASPT2 methods. The harmonic frequency  $\omega_e$ , the internuclear distance  $r_e$ , the rotational constant  $B_e$ , the electronic energy with respect to the ground state  $T_e$ , and the permanent dipole moment  $\mu$  have been calculated. By using the canonical functions approach, the eigenvalues  $E_v$ , the rotational constant  $B_v$  and the abscissas of the turning points  $r_{\min}$  and  $r_{\max}$  have been calculated for the considered electronic states up to the vibration level  $v = 12$ . Eleven electronic states have been studied theoretically here for the first time. The comparison of these values to the theoretical and experimental results available in literature shows a very good agreement.

**Keywords:** *Ab Initio* Calculation; NiO Molecule; Potential Energy Curves; Spectroscopic Constants; Dipole Moment; Rovibrational Calculation

## 1. Introduction

The metal oxide NiO shows complicated electronic spectra because of the presence of large number of electronic states derived from several low-lying configurations but it gives a systematic example of chemical bonding, which depends on the relative energy between the  $3d$  orbital of the metal and the  $2p$  orbital of oxygen [1,2]. The transition metal oxides have interesting applications in many fields such as materials application and the oxidation of metal surfaces. Among these compounds the NiO molecule which is considered as a prototype of ionic crystals, it is classified as a Mott-Hubbard insulator of very low conductivity. The conductivity of nanostructured NiO was found to be enhanced by six to eight orders of magnitude over those of NiO single crystals [3-10]. The magnetic properties of different sizes of NiO nanoparticles reveal the presence of superparamagnetism as evidenced by the increasing magnetization with decreasing size as well as the magnetic hysteresis at low temperatures. Nanomagnetism promises have applications in magnetic storage with nanomagnetic particles, improved battery lifetimes and also quantum computing [11-14]. The nanoarticles formed by the NiO molecule have many applications in electronics, optical, electro-optical devices and photo-

catalytic reaction. Despite this importance of the nickel oxide NiO, this molecule has been studied experimentally and theoretically [15-35] where a limited number of electronic states have been obtained with the corresponding molecular constants. The theoretical calculation of the NiO molecule is an extreme computational challenge because of the degeneracy of several energetically low-lying excited states and the open  $d$ ,  $p$ , and  $s$  shells. The presence of the  $d$  shell implies large multiplicities which are split by spin-orbit interaction. The components of the spin and the many states perturb each other. The prediction and assignment of the electronic configuration in the ground and excited states and the description of the bonding may often be difficult.

Based on our previous theoretical calculation [36-45], the important connection between energy relations of solids and molecules [46], and stimulated by the lack of theoretical calculation of excited electronic states with the existence of preliminary experimental and theoretical data, we performed an *ab initio* study of the low-lying electronic states of the molecule NiO below  $25,000\text{ cm}^{-1}$ . In this work, we investigate the potential energy curves (PECs), the electric dipole moment and spectroscopic constants for the 40  $2s+1\Lambda^{(\pm)}$  low-lying electronic states of this molecule obtained by MRCI and RSPT2 calculations. Taking advantage of the electronic structure of the inves-

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tigated electronic states of the NiO molecule and by using the canonical functions approach [47], the eigenvalues  $E_v$ , the rotational constant  $B_v$ , and the abscissas of the turning points  $r_{\min}$  and  $r_{\max}$  have been calculated for several vibrational levels of the considered electronic states.

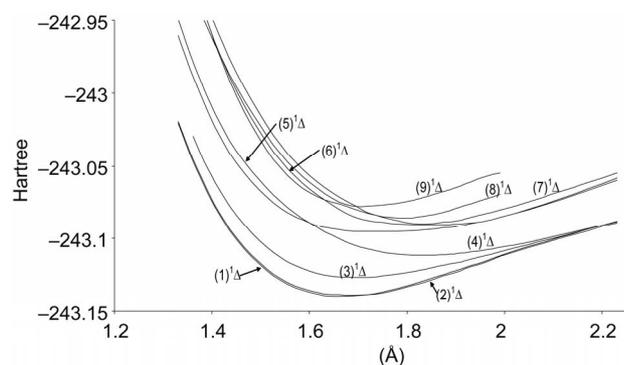
## 2. Computational Approach

### 2.1. *Ab Initio* Calculation

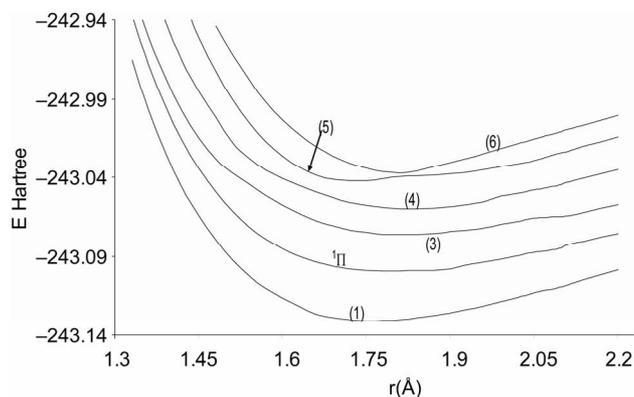
The PECs of the lowest-lying electronic states of the NiO molecule have been investigated via CASSCF and CASPT2 methods. The MRCI calculations (single and double excitations with Davidson corrections) were performed. The Nickel atom is treated as a system with 10 inner electrons taken into account using the basis LANL2DZ-ECP [48] for  $s$ ,  $p$  and  $d$  functions. The 8 electrons of the oxygen atom are considered using the DGauss-a<sub>2</sub>-Xfit [49] basis set including  $s$ ,  $p$  and  $d$  functions. Among the 26 electrons explicitly considered for the NiO molecule (18 electrons for Ni and 8 for O), 14 inner electrons were frozen in subsequent calculations so that 12 valence electrons were explicitly treated. This calculation has been performed via the computational chemistry program MOLPRO [50] taking advantage of the graphical user interface GABEDIT [51].

In the representation  $^{2s+1}\Lambda^{(\pm)}$ , 40 electronic states have been investigated for 46 internuclear distances in the range  $1.331 \text{ \AA} \leq r \leq 2.681 \text{ \AA}$  by using the MRCI and RSPT2 calculations. The potential energy curves for the singlet and triplet states, obtained by MRCI calculation, are given in **Figures 1-4**.

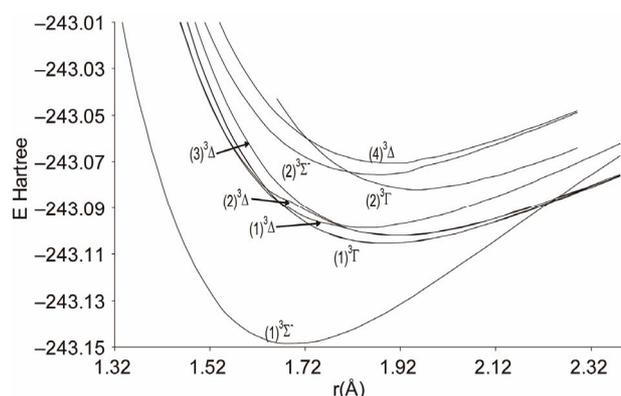
The spectroscopic constants such as the vibration harmonic constant  $\omega_e$ , the internuclear distance at equilibrium  $r_e$ , the rotational constant  $B_e$  and the electronic transition energy with respect to the ground state  $T_e$  have been calculated by fitting the energy values around the equilibrium position to a polynomial in terms of the internuclear distance. These values are given in **Table 1** together with the available data in the literature either theoretical or experimental.



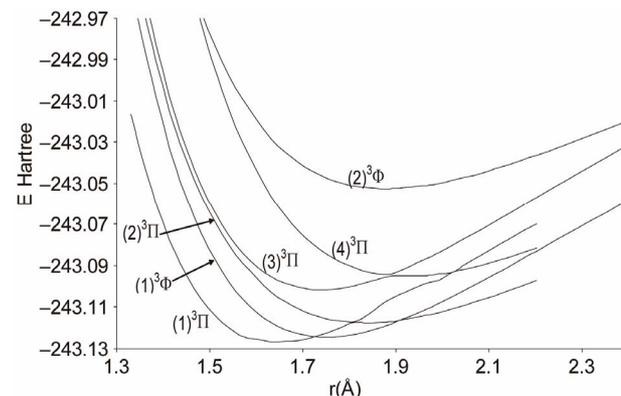
**Figure 1.** Potential energy curves of the lowest singlet  $^1\Delta$  and  $^1\Sigma$  states of the molecule NiO.



**Figure 2.** Potential energy curves of the lowest singlet  $^1\Pi$  states of the molecule NiO.



**Figure 3.** Potential energy curves of the lowest triplet  $^3\Sigma^-$ ,  $^3\Delta$  and  $^3T$  states the molecule NiO.



**Figure 4.** Potential energy curves of the lowest triplet  $^3\Pi$  and  $^3\Phi$  states of the molecule NiO.

An overlap between the  $3d$  and  $4s$  orbitals of the Ni atom and the  $2p$  orbitals of the oxygen atom lead to the formation of the molecular orbitals of the molecule NiO. The ground state of this molecule is confirmed theoretically and experimentally to be  $a^3\Sigma^-$  [1,16-23,34-35, 52-58], its electronic configuration can approximately described as  $8\sigma^2 3\pi^4 1\delta^4 9\sigma^2 4\pi^2$ . The  $9\sigma$  and  $4\pi$  orbitals are antibonding, the  $1\delta$  orbital is nonbonding, and the

**Table 1. Spectroscopic constants for the electronic states of the molecule NiO.**

States	$T_e$ (cm <sup>-1</sup> )	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )
$X^3\Sigma^-$	0.0 <sup>a1</sup>	1.690 <sup>a1</sup>	768.0 <sup>a1</sup>	0.469 <sup>a1</sup>
	0.0 <sup>a2</sup>	1.774 <sup>a2</sup>	634.6 <sup>a2</sup>	0.426 <sup>a2</sup>
	0.0 <sup>b1</sup>	1.627 <sup>b1</sup>		
	0.0 <sup>b2</sup>	1.626 <sup>b2</sup>	840 <sup>b2</sup>	
	0.0 <sup>b3</sup>		800(50) <sup>b3</sup>	
	0.0 <sup>b4</sup>	1.640 <sup>b4</sup>		
	0.0 <sup>b5</sup>	1.627 <sup>b5</sup>	839.1 <sup>b5</sup>	0.58 <sup>b5</sup>
	0.0 <sup>c</sup>		841 <sup>c</sup>	
	0.0 <sup>d</sup>	1.626 <sup>d</sup>	850 <sup>d</sup>	
	0.0 <sup>e</sup>	1.589 <sup>e</sup>	1068 <sup>e</sup>	
	0.0 <sup>g</sup>	1.631 <sup>g</sup>	838 <sup>g</sup>	
	0.0 <sup>h</sup>	1.627 <sup>h</sup>		
	0.0 <sup>i</sup>		839.69 <sup>i</sup>	
	0.0 <sup>j1</sup>	1.61 <sup>j1</sup>	876 <sup>j1</sup>	
	0.0 <sup>j2</sup>	1.60 <sup>j2</sup>	907 <sup>j2</sup>	0.5800(3) <sup>j</sup>
	0.0 <sup>j3</sup>	1.60 <sup>j3</sup>	903 <sup>j3</sup>	
	0.0 <sup>j4</sup>	1.64 <sup>j4</sup>	829 <sup>j4</sup>	
	0.0k	1.644 <sup>k</sup>	823 <sup>k</sup>	
	0.0 <sup>L1</sup>	1.682 <sup>L1</sup>	748 <sup>L1</sup>	
	0.0 <sup>L2</sup>	1.608 <sup>L2</sup>	906 <sup>L2</sup>	
0.0 <sup>L3</sup>	1.784 <sup>L3</sup>	848 <sup>L3</sup>		
0.0 <sup>m</sup>		615 <sup>m</sup>		
0.0 <sup>P</sup>		837.61 <sup>P</sup>		
		839.69 <sup>S</sup>		
(1) <sup>1</sup> $\Delta$	1956.3 <sup>a1</sup>	1.666 <sup>a1</sup>	802.4 <sup>a1</sup>	0.483 <sup>a1</sup>
(1) <sup>3</sup> $\Gamma$	2036.8 <sup>a2</sup>	1.921 <sup>a2</sup>	492.6 <sup>a2</sup>	0.363 <sup>a2</sup>
(2) <sup>1</sup> $\Delta$	2134.5 <sup>a1</sup>	1.681 <sup>a1</sup>	706.7 <sup>a1</sup>	0.475 <sup>a1</sup>
	2524.3 <sup>b1</sup>	1.66(1) <sup>b1</sup>		
(1) <sup>3</sup> $\Phi$	2305.8 <sup>a2</sup>	1.814 <sup>a2</sup>	624.2 <sup>a2</sup>	0.408 <sup>a2</sup>
<sup>1</sup> $\Pi$	2708.0 <sup>a2</sup>	1.890 <sup>a2</sup>	550.3 <sup>a2</sup>	0.375 <sup>a2</sup>
<sup>1</sup> $\Phi$ or <sup>1</sup> $\Pi$	3837.4 <sup>a1</sup>	1.752 <sup>a1</sup>	668.2 <sup>a1</sup>	0.437 <sup>a1</sup>
(1) <sup>1</sup> $\Gamma$	4243.7 <sup>a2</sup>	1.914 <sup>a2</sup>	529.7 <sup>a2</sup>	0.366 <sup>a2</sup>
(3) <sup>1</sup> $\Delta$	4779.3 <sup>a1</sup>	1.693 <sup>a1</sup>	685.8 <sup>a1</sup>	0.468 <sup>a1</sup>
<sup>1</sup> $\Delta$	4970.3 <sup>a2</sup>		485.3 <sup>a2</sup>	0.359 <sup>a2</sup>
(1) <sup>3</sup> $\Pi$	5068.6 <sup>a2</sup>	1.958 <sup>a2</sup>	435.8 <sup>a2</sup>	0.349 <sup>a2</sup>
<sup>3</sup> $\Pi_2$	3915.9 <sup>b1</sup>	1.645 <sup>b1</sup>		
<sup>3</sup> $\Pi_1$	4327.3 <sup>b1</sup>	1.645 <sup>b1</sup>		
<sup>3</sup> $\Pi$ ( $\Omega = 1$ )	4293.8 <sup>b2</sup>	1.644 <sup>b2</sup>	777 <sup>b2</sup>	
(1) <sup>3</sup> $\Pi_2$	3500.5 <sup>b3</sup>			
(1) <sup>3</sup> $\Pi_1$	3992.5 <sup>b3</sup>			
(1) <sup>3</sup> $\Pi_0$	4484.5 <sup>b3</sup>			
A <sup>3</sup> $\Pi_i$	4337.55546 <sup>h</sup>	1.6449 <sup>h</sup>	780.8 <sup>h</sup>	0.4970 <sup>h</sup>
<sup>3</sup> $\Pi$	4293.78(5) <sup>j</sup>		777.10(5) <sup>j</sup>	0.49701(2) <sup>j</sup>
<sup>3</sup> $\Pi$		1.633 <sup>c</sup>	947 <sup>c</sup>	
<sup>3</sup> $\Pi$			540 <sup>q</sup>	
<sup>3</sup> $\Pi$	3260 <sup>n</sup>			

## Continued

$^3\Pi$		1.64 <sup>i</sup>	787 <sup>i</sup>	
(2) $^3\Phi$	5271.9 <sup>a1</sup>	1.749 <sup>a1</sup>	692.6 <sup>a1</sup>	0.4382 <sup>a1</sup>
	5230.6 <sup>b1</sup>	1.66(2) <sup>b1</sup>		
$^3\Phi$ ( $\Omega = 4$ )	3468.3 < $\Gamma_e$ < 4274.8 <sup>b2</sup>			
$^3\Phi$ ( $\Omega = 3$ )	5250.8 <sup>b2</sup>			
$^3\Phi$ ( $\Omega = 2$ )	6218.7 <sup>b2</sup>			
(1) $^1\Pi$	5664.91 <sup>a1</sup>	1.642 <sup>a1</sup>	727.6 <sup>a1</sup>	0.4982 <sup>a1</sup>
(2) $^3\Pi$	6790.9 <sup>a1</sup>	1.835 <sup>a1</sup>	544.4 <sup>a1</sup>	0.3981 <sup>a1</sup>
( $^3\Phi_4, ^3\Delta_3, ^3\Pi_2$ )	7659.2 <sup>b1</sup>	1.66(2) <sup>b1</sup>		
( $^3\Phi_3, ^3\Delta_2, ^3\Pi_1$ )	8232.7 <sup>b1</sup>	1.66(2) <sup>b1</sup>		
( $^3\Phi_2, ^3\Delta_1, ^3\Pi_0$ )	8788.4 <sup>b1</sup>	1.66(2) <sup>b1</sup>		
$^3\Pi$	$\approx 6000^c$			
(4) $^1\Delta$	8091.0 <sup>a1</sup>	1.829 <sup>a1</sup>	581.6 <sup>a1</sup>	0.4008 <sup>a1</sup>
$^1\Delta$	7581.2 <sup>b2</sup>	1.600(6) <sup>b2</sup>	615(15) <sup>b2</sup>	
a( $^1\Delta$ )	7614.1 <sup>b3</sup>		680(60) <sup>b3</sup>	
(1) $^3\Gamma$	9454.1 <sup>a1</sup>	1.887 <sup>a1</sup>	539.7 <sup>a1</sup>	0.3764 <sup>a1</sup>
(2) $^3\Gamma$	9471.6 <sup>a1</sup>	1.887 <sup>a1</sup>	540.7 <sup>a1</sup>	0.3765 <sup>a1</sup>
(3) $^3\Pi$	10 276.4 <sup>a1</sup>	1.740 <sup>a1</sup>	714.4 <sup>a1</sup>	0.4425 <sup>a1</sup>
(3) $^3\Pi$	9552.7 <sup>a2</sup>	1.795 <sup>a2</sup>	804.8 <sup>a2</sup>	0.4163 <sup>a2</sup>
$^3\Pi$ ( $\Omega = 0$ )	9449.1 <sup>b2</sup>			
$^3\Pi$ ( $\Omega = 1$ )	9848.5 <sup>b2</sup>	1.66(2) <sup>b1</sup>		
$^3\Pi$ ( $\Omega = 2$ )	10090.2 <sup>b2</sup>			
(1) $^3\Delta$	10185.1 <sup>a1</sup>	1.917 <sup>a1</sup>	598.1 <sup>a1</sup>	0.3648 <sup>a1</sup>
$^3\Delta$		1.616 <sup>c</sup>	991 <sup>c</sup>	
$^3\Delta$			580 <sup>d</sup>	
(2) $^3\Delta$	10243.65 <sup>a1</sup>	1.918 <sup>a1</sup>	504.7 <sup>a1</sup>	0.3642 <sup>a1</sup>
(2) $^1\Pi$	10823.3 <sup>a1</sup>	1.807 <sup>a1</sup>	448.7 <sup>a1</sup>	0.4101 <sup>a1</sup>
$^1\Pi_1$	10095.1 <sup>b1</sup>	1.66(2) <sup>b1</sup>		
(3) $^3\Delta$	10945.1 <sup>a1</sup>	1.850 <sup>a1</sup>	683.5 <sup>a1</sup>	0.3918 <sup>a1</sup>
(5) $^1\Delta$	11690.0 <sup>a1</sup>	1.737 <sup>a1</sup>	419.8 <sup>a1</sup>	0.4459 <sup>a1</sup>
(4) $^3\Pi$	11723.3 <sup>a1</sup>	1.922 <sup>a1</sup>	556.7 <sup>a1</sup>	0.3630 <sup>a1</sup>
$^1\Sigma^+$	11803.4 <sup>a2</sup>	1.902 <sup>a2</sup>	528.5 <sup>a2</sup>	0.371 <sup>a2</sup>
(6) $^1\Delta$	12686.6 <sup>a1</sup>	1.840 <sup>a1</sup>	382.9 <sup>a1</sup>	0.3940 <sup>a1</sup>
(6) $^1\Delta$	12687.6 <sup>a2</sup>	1.939 <sup>a2</sup>	569.8 <sup>a2</sup>	0.3560 <sup>a2</sup>
(7) $^1\Delta$	12852.8 <sup>a1</sup>	1.835 <sup>a1</sup>	813.9 <sup>a1</sup>	0.3982 <sup>a1</sup>
(8) $^1\Delta$	13715.2 <sup>a1</sup>	1.798 <sup>a1</sup>	904.78 <sup>a1</sup>	0.4146 <sup>a1</sup>
(3) $^3\Phi$	13911.9 <sup>a2</sup>	1.901 <sup>a2</sup>	541.15 <sup>a2</sup>	0.3707 <sup>a2</sup>
B( $^3\Phi$ )	10 025.7 <sup>b3</sup>			
$^1\Sigma^+$	14 595.5 <sup>a1</sup>	1.967 <sup>a1</sup>	533.1 <sup>a1</sup>	0.3462 <sup>a1</sup>
b1( $^1\Sigma^+$ )	14526.4 <sup>b3</sup>			
$^1\Sigma^+$		1.669 <sup>c</sup>	864 <sup>c</sup>	
$^1\Sigma^+$			560 <sup>q</sup>	
$^1\Phi$	15460.2 <sup>a2</sup>	1.901 <sup>a2</sup>	536.53 <sup>a2</sup>	0.371 <sup>a2</sup>
$^1\Pi$	15923.6 <sup>a1</sup>	1.815 <sup>a1</sup>	594.2 <sup>a1</sup>	0.4066 <sup>a1</sup>
(2) $^3\Sigma^-$	16053.6 <sup>a1</sup>	1.870 <sup>a1</sup>		
$^3\Sigma^-$	16000.0 <sup>i</sup>			
A $^3\Sigma^-$	16075.0 <sup>s</sup>		617.0 <sup>s</sup>	

## Continued

(4) <sup>3</sup> Δ	17094.3 <sup>a1</sup>	1.904 <sup>a1</sup>	528.9 <sup>a1</sup>	0.3695 <sup>a1</sup>
<sup>3</sup> Δ		1.616 <sup>c</sup>	991 <sup>c</sup>	
<sup>3</sup> Δ			580 <sup>g</sup>	
(3) <sup>1</sup> Π	19452.6 <sup>a1</sup>	1.830 <sup>a1</sup>	639.8 <sup>a1</sup>	0.4001 <sup>a1</sup>
<sup>1</sup> Π	19447.3 <sup>a2</sup>	1.775 <sup>a2</sup>	641.1 <sup>a2</sup>	0.4256 <sup>a2</sup>
( <sup>1</sup> Π)	19204.5 <sup>b3</sup>			
<sup>1</sup> Π	20828.2 <sup>a2</sup>	1.867 <sup>a2</sup>	617.6 <sup>a2</sup>	0.3848 <sup>a2</sup>
(4) <sup>3</sup> Φ	21073.1 <sup>a1</sup>	1.879 <sup>a1</sup>	541.3 <sup>a1</sup>	
<sup>1</sup> Π	23088.9 <sup>a2</sup>	1.897 <sup>a2</sup>	537.2 <sup>a2</sup>	0.3725 <sup>a2</sup>
<sup>1</sup> Φ	24177.4 <sup>a2</sup>	1.909 <sup>a2</sup>	618.0 <sup>a2</sup>	0.3671 <sup>a2</sup>
<sup>1</sup> Π	24600.9 <sup>a2</sup>	1.951 <sup>a2</sup>	544.0 <sup>a2</sup>	0.3525 <sup>a2</sup>

<sup>a1</sup>For the present work with MRCI calculation; <sup>A2</sup>For the present work with CASPT2 calculation; <sup>b1</sup>Ref. 52; <sup>b2</sup>Ref. 53; <sup>b3</sup>Ref. 54; <sup>b4</sup>Ref. 55; <sup>b5</sup>Ref. 17; <sup>c</sup>Ref. 20; <sup>d</sup>Ref. 56; <sup>e</sup>Ref. 24; <sup>f</sup>Ref. 1; <sup>h</sup>Ref. 19; <sup>i</sup>Ref. 18; <sup>j1(NRel)</sup>Ref. 57; <sup>j2(Xω)</sup>Ref. 57; <sup>j3(VWN)</sup>Ref. 57; <sup>j4(GC)</sup>Ref. 57; <sup>k</sup>Ref. 34; <sup>L1(SCF)</sup>Ref. 23; <sup>L2(Cl(SD))</sup>Ref. 23; <sup>L2(+Q)</sup>Ref. 23; <sup>m</sup>Ref. 35; <sup>n</sup>Ref. 21; <sup>p</sup>Ref. 16; <sup>q</sup>Ref. 22; <sup>s</sup>Ref. 58.

remaining orbitals are bonding [53]. The electronic structure of all the open shell  $3d$  oxide are dominated by  $M^{2+}O^{2-}$  zero-order character at low energy, while the NiO molecule has the chance to be represented by  $Ni^+O^-$  atomic-ion-in-molecule model [18]. Our calculated values of the internuclear distance  $r_e$  and the vibrational harmonic constant  $\omega_e$ , for the ground state, by using the MRCI calculation, are in very good agreement with the experimental values in literature with the relative differences 2.7% (Ref. [34])  $< \Delta r_e/r_e < 3.8%$  (Ref. [53]) and 4% (Ref. [53])  $< \Delta \omega_e/\omega_e < 8.5%$  (Ref. [18]) respectively. These relative differences become larger by using the CASPT2 method where 7.3% (Ref. [34])  $< \Delta r_e/r_e < 8.3%$  (Ref. [53]) and 20.6% (Ref. [54])  $< \Delta \omega_e/\omega_e < 24.4%$  (Ref. [18]), but the value of  $\omega_e$  given by Huber and Herzberg [35] is in very good agreement with our value calculated by CASPT2 method where  $\Delta \omega_e/\omega_e = 3%$  and bad agreement with the value calculated by the MRCI method with  $\Delta \omega_e/\omega_e = 20%$ . By comparing our calculated values of  $r_e$  with those calculated theoretically in literature we obtained a very good agreement with relative differences 3.8% (Ref. [56])  $< \Delta r_e/r_e < 5.6%$  (Ref. [23]) and 0.5% (Ref. [23])  $< \Delta r_e/r_e < 8.3%$  (Ref. [56]) calculated by MRCI and CASPT2 respectively, while the theoretical values of  $\omega_e$  calculated in literature varies between 748 and 1068  $cm^{-1}$  and our values are in agreement with the lower value.

A large number of low-lying electronic states, many with very high spin multiplicity, of  $3d$  metal oxides are produced by the unpaired electrons, therefore strong state mixing results in spectroscopy which implies difficult theoretical calculation. Another dimension of complexity can be added originating for the large nuclear spin and magnetic moment of the nuclei with odd atomic number. The first excited state of the NiO molecules has long been a matter of controversy. The theoretical calculation of Bauschlicher Jr. and collaborators [21,22,56] and that

of Bakalbassis *et al.* [24] found that the first excited state of this molecule is  $^3\Pi$ . Moravec and Jarrold [53] and Wu and Wang [54] confirmed experimentally that  $^3\Pi$  is the first excited state. For Ram and Bernath [19] and Freidman-Hill and Field [18] this  $^3\Pi$  state is located experimentally above the ground state  $X^3\Sigma^-$  at 4330 and 4293  $cm^{-1}$  respectively. From the photoelectron spectroscopy technique, Ramond *et al.* located the  $^3\Pi_2$  and  $^3\Pi_1$  at 3916 and 4327  $cm^{-1}$  respectively [52]. By a theoretical calculation, Walch and Goddard [20] predicted that the first excited state is  $^1\Pi$  rather than  $^3\Pi$  and located this state at 6000  $cm^{-1}$  above the ground state  $X^3\Sigma^-$ . This prediction of Walch and Goddard [20] for the first excited state  $^1\Delta$  is in agreement with the present work but our  $^3\Pi$  state is located at 5068.6  $cm^{-1}$  above the ground state. Moreover between the first excited state  $(1)^1\Delta$  and the  $(1)^3\Pi$  we found the 4 new singlet electronic states  $(1)^1\Delta$ ,  $(2)^1\Delta$ ,  $^1\Phi$  or  $^1\Pi$  and  $(3)^1\Delta$  by using MRCI calculation and the 2 new triplet electronic states  $(1)^3\Gamma$ ,  $(1)^3\Phi$ , and the 3 new singlet electronic states  $^1\Pi$  ( $1^1\Pi$  and  $^1\Delta$ ) by using RSPT2 calculation. The agreement between the 2 ways of calculation is only for the last state  $^1\Delta$ . Ramond *et al.* [52] investigated an electronic state at 2525  $cm^{-1}$  between  $X^3\Sigma^-$  and  $^3\Pi_2$  states without assigning the nature of this state. By comparing the data of this state with our calculated values, one can find that, it is either  $(2)^1\Delta$  or  $(1)^3\Phi$ .

Also without assigning the name of the state, Ramond *et al.* [52] detected the energy 5230.6  $cm^{-1}$  above the  $^3\Pi_1$ , this energy is in very good agreement with the energy of our calculated  $(2)^3\Phi$  state with the relative differences  $\Delta T_e/T_e = 0.8%$  and  $\Delta r_e/r_e = 5%$ . Between the values of energy 7659.2  $cm^{-1} < T_e < 8788.4 cm^{-1}$ , Ramond *et al.* [52] suggested to these values an assignment to one of the three states  $^3\Phi_i$ ,  $^3\Delta_i$  and  $^3\Pi_i$ . By comparing this data to our calculated values in the present work (**Table 1**), the assignment to the states  $^3\Phi_1$  and  $^3\Delta_1$  are excluded since  $T_e((2)^3\Phi = 5271.9 cm^{-1})$ ,  $T_e((3)^3\Phi = 13911.9 cm^{-1})$ ,

$T_e((1)^3\Delta = 10185.1 \text{ cm}^{-1})$ , and  $T_e((2)^3\Delta = 10243.65 \text{ cm}^{-1})$ , therefore the only possible assignment is  $(2)^3\Pi$ . These values of energy obtained by Ramond *et al.* [52] can fit also with the energy of the state  $(4)^1\Delta$  in **Table 1**, but since this state is not suggested by the authors, this assignment is excluded in the present work. The same authors [52] obtained experimentally for the state  $^1\Pi$  the energy  $T_e = 10095.1 \text{ cm}^{-1}$  which fits with our calculated value of the state  $(2)^1\Pi$  with the relative difference  $\Delta T_e/T_e = 6.7\%$ .

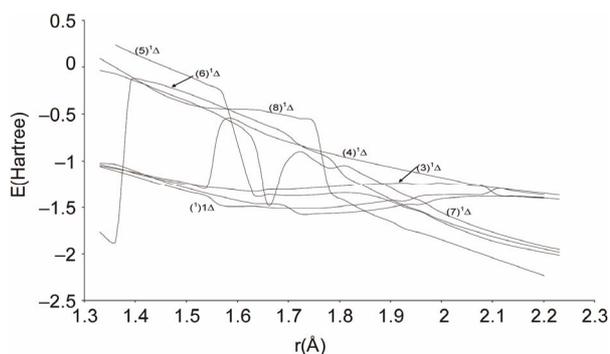
The values of the energy  $T_e$  of the states  $^3\Phi_{2,3,4}$  and  $^1\Delta$  obtained experimentally by Moravec and Jarrold [53] are respectively in good agreement and assignment with the  $(2)^3\Phi$  and  $(4)^1\Delta$  of the present work. Our calculated value of  $\omega_e$  for the state  $(4)^1\Delta$  is in good agreement with that measured by Moravec and Jarrold [53] with relative difference  $\Delta\omega_e/\omega_e = 5.4\%$ . The  $^3\Pi_{1,2,3}$  states detected by Moravec and Jarrold [53] are in good agreement and assignment with the  $(3)^3\Pi$  of the present work (**Table 1**).

The assignment of the three states  $a(^1\Delta)$ ,  $b(^1\Sigma^+)$  and  $c(^1\Pi)$  detected experimentally by Wu and Wang [54] are in very good agreement with our assignment of the states  $(4)^1\Delta$ ,  $^1\Sigma^+$  and  $(3)^1\Pi$  with the relative differences  $\Delta T_e/T_e$  ( $a(^1\Delta)$ ) = 6%,  $\Delta T_e/T_e$  ( $b(^1\Sigma^+)$ ) = 0.5%,  $\Delta T_e/T_e$  ( $c(^1\Pi)$ ) = 1.3% respectively. Bauschlicher Jr. [21] calculated the nearest  $^1\Sigma^+$  state at  $8340 \text{ cm}^{-1}$  above the  $^3\Sigma^-$  which is in disagreement with our calculated value and those of Wu and Wang [54]. The MRCI calculated values of  $T_e$ , in the present work, for the  $(2)^3\Phi$  and  $(3)^3\Phi$  states are respectively  $5271.9$  and  $13911.9 \text{ cm}^{-1}$ , therefore the possible assignment of the  $B(^3\Phi)$  state, where  $T_e = 10025.7 \text{ cm}^{-1}$ , investigated by Wu and Wang [54] is the  $(3)^3\Phi$  (**Table 1**). The calculated values of  $r_e$  and  $\omega_e$  by Bakalbassiss *et al.* [24] for the states  $^3\Delta$  and  $^1\Sigma^+$ , which are fitting with our  $(4)^3\Delta$  and  $^1\Sigma^+$ , are in disagreement with the values calculated in the present work, while there are good agreements between our data and those of Bauschlicher Jr. and Maitre [56] for the values of  $r_e$  for these states with the relative differences  $\Delta r_e/r_e(^3\Delta) = 9\%$  and  $\Delta r_e/r_e(^1\Sigma^+) = 5\%$ .

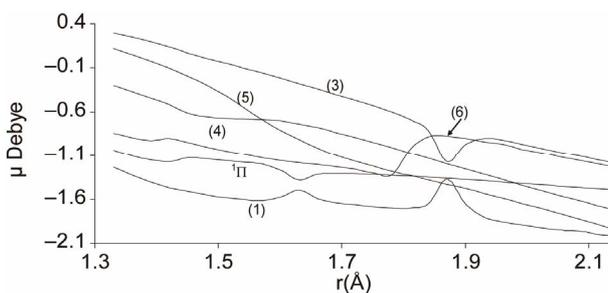
The  $^3\Sigma^-$  at  $16,000 \text{ cm}^{-1}$  predicted by Friedman-Hill and Field [18] is in very good agreement with the  $(2)^3\Sigma^-$  state calculated in the present work with the relative difference  $\Delta T_e/T_e = 0.3\%$ . The detected  $^3\Pi$  state by Walch and Goddard [20] at  $\approx 6000 \text{ cm}^{-1}$  fits with our assignment of the state  $(2)^3\Pi$  where the relative difference in energy  $\Delta T_e/T_e = 12\%$ . The comparison of our results with the most recent investigation on the molecule NiO [58] shows an excellent agreement with our results for the state  $^3\Sigma^-$ , but our assumption for the energies  $19452.6 \text{ cm}^{-1}$  and  $19447.3 \text{ cm}^{-1}$  are in agreement with that given by Wu and Wang [54]. Because of the breakdown of the Born-Oppenheimer approximation at the crossing and avoided crossing of the potential energy curves near the minimum of the potential energy curves there is no cal-

ulation of the spectroscopic constants of other calculated electronic states where the potential energy curves are given in **Figures 1-4**.

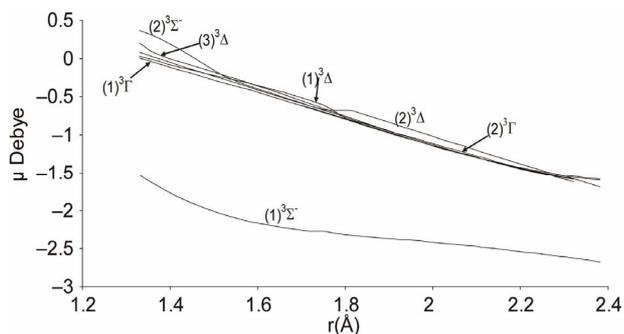
The electric dipole moment is an effective gauge of the ionic characters; it is helping for understanding the macroscopic properties of imperfect gases, liquids and solids and is of great utility in the construction of molecular orbital. The expectation value of this operator is sensitive primarily to the nature of the least energetic and most chemically relevant valence electrons. To understand the ionic behavior of the excited electronic states we have presented in **Figures 5-8** the adiabatic permanent dipole moment for the investigated electronic states in the range of the considered internuclear distance. It was seen that the variation of the adiabatic dipole moment is very important in the vicinity of the avoided crossings and the position of the peaks corresponds to the positions of these avoided crossings of the adiabatic curves. Each time an adiabatic state loses its ionic character, it becomes neutral and the corresponding dipole moment tends towards zero. One can notice the fit between the positions of the intersections of the permanent dipole moment curves and the position of the avoided crossings of the corresponding potential energy curves for the following states  $(4)^1\Delta/(5)^1\Delta$ ,  $(6)^1\Delta/(7)^1\Delta$  and  $(1)^3\Delta/(3)^3\Delta$  at  $1.631 \text{ \AA}$ ,  $1.812 \text{ \AA}$  and  $1.811 \text{ \AA}$  respectively. These fittings confirm the validity and the accuracy of the investigated data in the present work on the molecule NiO.



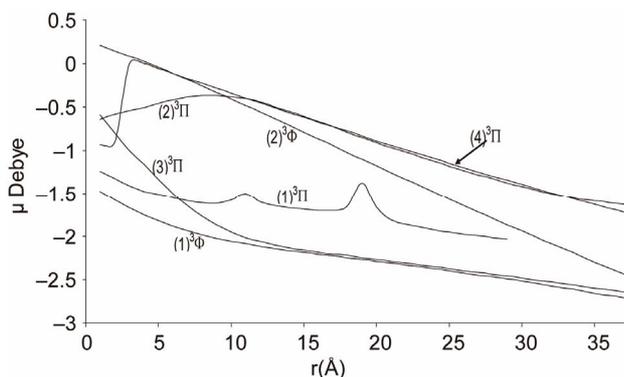
**Figure 5.** Permanent dipole moment curves of the lowest singlet  $^1\Delta$  and  $^1\Sigma$  states of the molecule NiO.



**Figure 6.** Permanent dipole moment curves of the lowest singlet  $^1\Pi$  states of the molecule NiO.



**Figure 7.** Permanent dipole moment curves of the lowest singlet  $^3\Sigma^-$ ,  $^3\Delta$  and  $^3\Gamma$  states of the molecule NiO.



**Figure 8.** Permanent dipole moment curves of the lowest triplet  $^3\Pi$  and  $^3\Phi$  states of the molecule NiO.

## 2.2. The Vibration-Rotation Calculation

Within the Born-Oppenheimer approximation, the vibration rotation motion of a diatomic molecule in a given electronic state is governed by the radial Schrödinger equation

$$\left[ \frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2} (E_{v,J} - U(r)) - \frac{\lambda}{r^2} \right] \Psi_{v,J}(r) = 0 \quad (1)$$

where  $r$  is the internuclear distance,  $v$  and  $J$  are respectively the vibrational and rotational quantum numbers,  $\lambda = J(J+1)$ ,  $E_{v,J}$  and  $\Psi_{v,J}$  are respectively the eigenvalue and the eigenfunction of this equation. In the perturbation theory these functions can be expanded as

$$E_{v,J} = \sum_{n=0} e_n \lambda^n \quad (2)$$

$$\Psi_{v,J}(r) = \sum_{n=0} \Phi_n(r) \lambda^n \quad (3)$$

with  $e_0 = E_v$ ,  $e_1 = B_v$ ,  $e_2 = -D_v$ ,  $\phi_0$  is the pure vibration wave function and  $\phi_n$  its rotational corrections. By replacing Equations (2) and (3) into Equation (1) and since this equation is satisfied for any value of  $\lambda$ , one can write [47,59-63]

$$\phi_0''(r) + [e_0 - U(r)] \phi_0(r) = 0 \quad (4)$$

$$\phi_1''(r) + [e_0 - U(r)] \phi_1(r) = -[e_1 - R(r)] \phi_0(r) \quad (5a)$$

$$\phi_2''(r) + [e_0 - U(r)] \phi_2(r) = -[e_1 - R(r)] \phi_1(r) - e_2 \phi_0(r) \quad (5b)$$

...

$$\phi_n''(r) + [e_0 - U(r)] \phi_n(r) = R(r) \phi_{n-1} - \sum_{m=1}^n e_m \phi_{n-m}(r) \quad (5n)$$

where  $R(r) = 1/r^2$ , the first equation is the pure vibrational Schrödinger equation and the remaining equations are called the rotational Schrödinger equations. One may project Equations (7) onto  $\phi_0$  and find

$$\langle \phi_0 | \phi_0 \rangle e_1 = \left\langle \phi_0 \left| \frac{1}{r^2} \right| \phi_0 \right\rangle \quad (6a)$$

$$\langle \phi_0 | \phi_0 \rangle e_2 = \left\langle \phi_0 \left| \frac{1}{r^2} \right| \phi_1 \right\rangle - e_1 \langle \phi_0 | \phi_1 \rangle \quad (6b)$$

...

$$\langle \phi_0 | \phi_0 \rangle e_n = \left\langle \phi_0 \left| \frac{1}{r^2} \right| \phi_{n-1} \right\rangle - \sum_{m=1}^{n-1} e_m \langle \phi_{n-m} | \phi_0 \rangle \quad (6n)$$

Once  $e_0$  is calculated from Equation (4),  $e_1$ ,  $e_2$ ,  $e_3 \dots$  can be obtained by using alternatively Equations (5) and (6). By using the canonical functions approach [47] and the cubic spline interpolation between each two consecutive points of the PECs obtained from the *ab initio* calculation of the NiO molecule, the eigenvalue  $E_v$ , the rotational constant  $B_v$ , the distortion constant  $D_v$ , and the abscissas of the turning point  $r_{\min}$  and  $r_{\max}$  have been calculated up to the vibrational levels  $v = 12$  for the investigated electronic states in the present work. These values for the state  $X^1\Sigma^+$  and the  $(2)^3\Phi$  (as illustration) are given in **Table 2**. The comparison of the investigated values of  $B_v$  and  $D_v$  in literature [18,19,25] with our calculated values for these states showed a good agreement with relative difference  $\Delta B_v/B_v \approx 8\%$  for  $v = 0, 1$  and  $\Delta D_v/D_v$  equal 7.5% and 2.4 % respectively for  $v = 1$  and  $v = 2$ .

## 3. Conclusion

In the present work, the *ab initio* investigation for the 40 low-lying singlet and triplet electronic states of the NiO molecule has been performed via CAS-SCF/MRCI and CASPT2 methods. The potential energy and the dipole moment curves have been determined along with the spectroscopic constants  $T_e$ ,  $r_e$ ,  $\omega_e$ , and the rotational constant  $B_e$  for the lowest-lying electronic states. The comparison of our results, for different states, with those obtained experimentally and theoretically shows a good agreement. By using the canonical functions approach [47,59-63], the eigenvalue  $E_v$ , the rotational constant  $B_v$ ,

**Table 2. Rovibrational calculation of the  $X^3\Sigma^-$  and  $(2)^3\Phi$  of the molecule NiO.**

$X^3\Sigma^-$					
V	$E_v$ (cm <sup>-1</sup> )	$B_v \times 10$ (cm <sup>-1</sup> )	$D_v \times 10^7$ (cm <sup>-1</sup> )	$R_{\min}$ (Å)	$R_{\max}$ (Å)
0	383.3	4.66 <sup>a1</sup>	6.83 <sup>a1</sup>	1.638	1.750
		5.05823(11) <sup>h</sup>	7.387 <sup>h</sup>		
		5.05836 <sup>r</sup>	7.48 <sup>r</sup>		
		5.0369 <sup>i</sup>			
1	1147.8	4.61	7.64	1.600	1.808
		5.01488(49) <sup>h</sup>	7.46(44) <sup>h</sup>		
		5.01544 <sup>r</sup>	7.52 <sup>r</sup>		
2	1880.5	4.58	5.83	1.577	1.845
3	2631.2	4.54	7.55	1.558	1.877
4	3360.9	4.49	5.50	1.544	1.906
5	4097.3	4.46	7.48	1.531	1.933
6	4817.6	4.42	5.34	1.521	1.958
7	5539.5	4.38	6.88	1.511	1.983
8	6250.2	4.34	6.68	1.502	2.006
9	6952.3	4.30	7.13	1.493	2.030
10	7644.4	4.27	7.27	1.485	2.052
11	8327.0	4.24	7.17	1.478	2.074
$(2)^3\Phi$					
0	276.6	4.45	1.11	1.696	1.806
1	842.8	4.48	1.05	1.660	1.854
2	1420.9	4.50	1.40	1.640	1.890
3	1975.3	4.53	1.33	1.617	1.919
4	2524.8	4.55	1.63	1.602	1.946

<sup>a1</sup>Present work with MRCI calculation; <sup>h</sup>Ref. 19; <sup>r</sup>Ref. 25; <sup>i</sup>Ref. 18.

and the abscissas of the turning points  $r_{\min}$  and  $r_{\max}$  have been calculated up to the vibrational level  $v = 12$ . Eleven electronic states have been investigated in the present work for the first time.

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