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Theoretical Calculation of the Low-Lying Electronic States of the Molecule PbO

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Abstract

The potential energy curves of the lowest 20 electronic states in the representation $^{2s+1}\Lambda^{(\pm)}$ of the molecule PbO have been investigated via *ab initio* CASSCF and MRCI (single and double excitations with Davidson correction) calculations. The spectroscopic constants such as vibrational harmonic frequency ω_e, the internuclear distance at equilibrium R_e, the rotational constant B_e, and the electronic transition energy T_e with respect to the ground state have been calculated along with the permanent dipole moment for the different bound investigated electronic states. 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. The comparison of these values with those available in the literature shows a very good agreement.

Keywords

***Ab Initio* Calculation, PbO Molecule, Potential Energy Curves, Spectroscopic Constants, Dipole Moment, Rovibrational Calculation**

1. Introduction

The lead metal monoxide was the subject of many experimental investigations [1] [2] and several theoretical studies [3]-[7]. It is one of the most technologically important oxide materials which is used in the manufacture of different ceramics products. Because of its electrical and electronic properties, it is used in capacitors and electrophotographic plates, as well as in ferromagnetic and ferroelectric materials. It is also used as an activator in rubber, in oil refining, as an oxidation catalyst in several organic chemical processes, in the production of many lead chemicals, dry colors, soaps, and driers for paint. Moreover it is used in the production of lead salts,

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particularly those used as stabilizers for plastics, notably polyvinyl chloride materials.

There is a rapid increase and concern in studying the spectra of this molecule which is shown in the different papers written on its low lying electronic states. It has been experimentally proven that the ground state of the molecule PbO is $^1\Sigma^+$ [8]-[10]. This result has been theoretically confirmed in a number of studies that used different methods [3]-[14]. The three excited electronic states $B^3\Pi$, $A^3\Pi$, and $a^3\Sigma^+$ have been investigated by Oldenborg *et al.* [9] while the electric-dipole moment of $(1)^3\Sigma^+$ state of PbO molecule has been measured by Hunter *et al.* [15]. By using the CASSCF/CASPT calculation the six electronic states $^3\Sigma^\pm$, $^1\Sigma^-$, $^{1,2}\Delta$, and $^3\Pi$ of this molecule have been investigated without [12] and with spin orbit coupling [16].

In the present work 20 low-lying singlet and triplet electronic states of PbO molecule have been investigated by using the *ab initio* method using two basis sets. The potential energy curves (PECs) together with the transition energy with respect to the minimum energy for the ground state T_e, the equilibrium internuclear distance R_e, the harmonic frequency ω_e, the rotational constant B_e, and the permanent dipole moment (DMCs) μ have been obtained for the considered electronic states. Nine and eleven electronic states have been investigated here for the first time using respectively the first and the second basis sets. Taking advantage of the electronic structure of the investigated electronic states of the molecule PbO and by using the canonical functions approach, the eigenvalue E_v, the rotational constant B_v, and the turning points $R_{\min}$ and $R_{\max}$ have been calculated for several vibrational levels of the considered singlet and triplet electronic states.

2. Method of Calculations

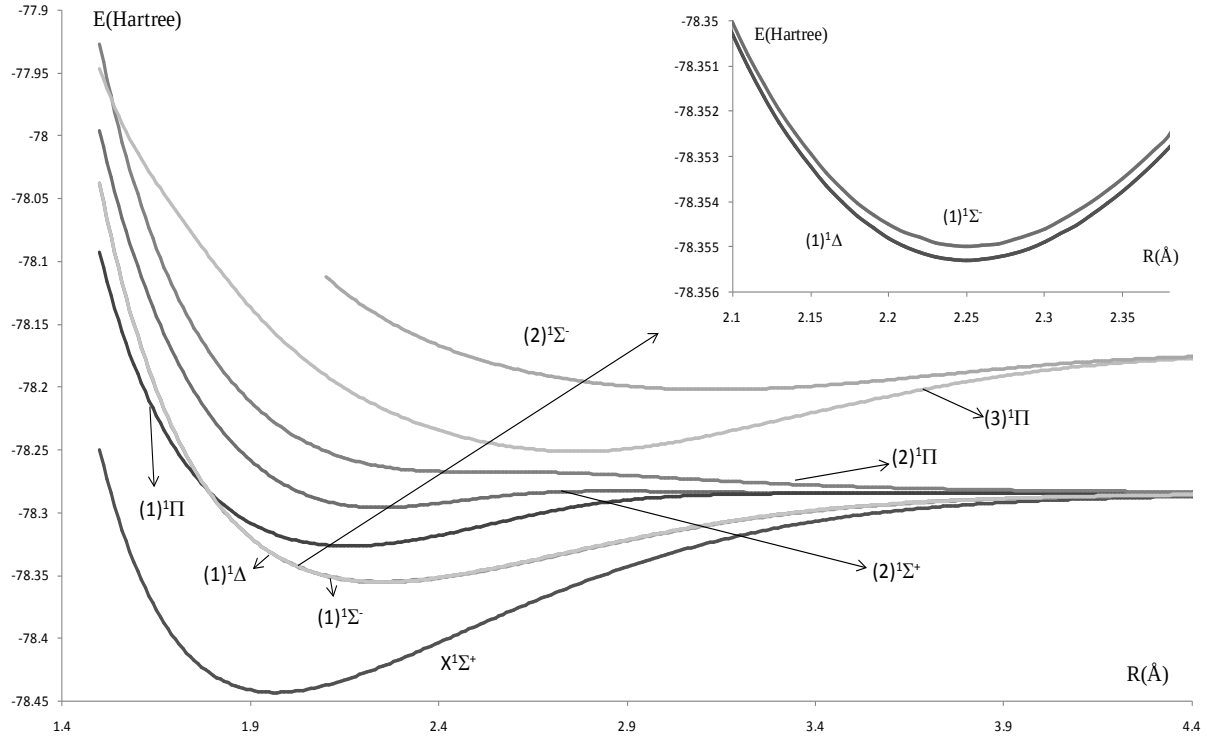
2.1. *Ab Initio* Calculation

In the present work we study the low-lying singlet and triplet electronic states of the molecule PbO using state averaged complete active space self consistent field (CASSCF) procedure followed by a multireference configuration interaction (MRDSCI+Q with Davidson correction) treatment for the electron correlation. The entire CASSCF configuration space was used as the reference in the MRDSCI calculations, which were done via the computational chemistry program MOLPRO [17] taking advantage of the graphical user interface GABEDIT [18]. Since we noticed large discrepancies between the calculated values of ω_e in literature, two different ways have been used in the present theoretical study of the PbO molecule. In the first and the second ways the 82 electrons of the lead atom are considered using the effective core potential ECP78MWB basis set for s, p, and d functions. While the oxygen species is treated as a system of 8 electrons by using, for the s, p, and d functions, the 6-311++G** and the DGauss-a2-X fit basis sets respectively for the first and the second ways respectively. For these 2 ways of calculation the potential energy curves and the static dipole moments of the low-lying electronic states of the molecule PbO were generated using the MRSDCI+Q for 350 internuclear distances calculations in the range 1.5 Å $\le R_e \le$ 5.0 Å in the representation $^{2s+1}\Lambda^{(\pm)}$ where we assumed that, the PbO molecule is mainly ionic around the equilibrium position. These PECs and the DMCs for the different symmetries are given in **Figures 1-4**.

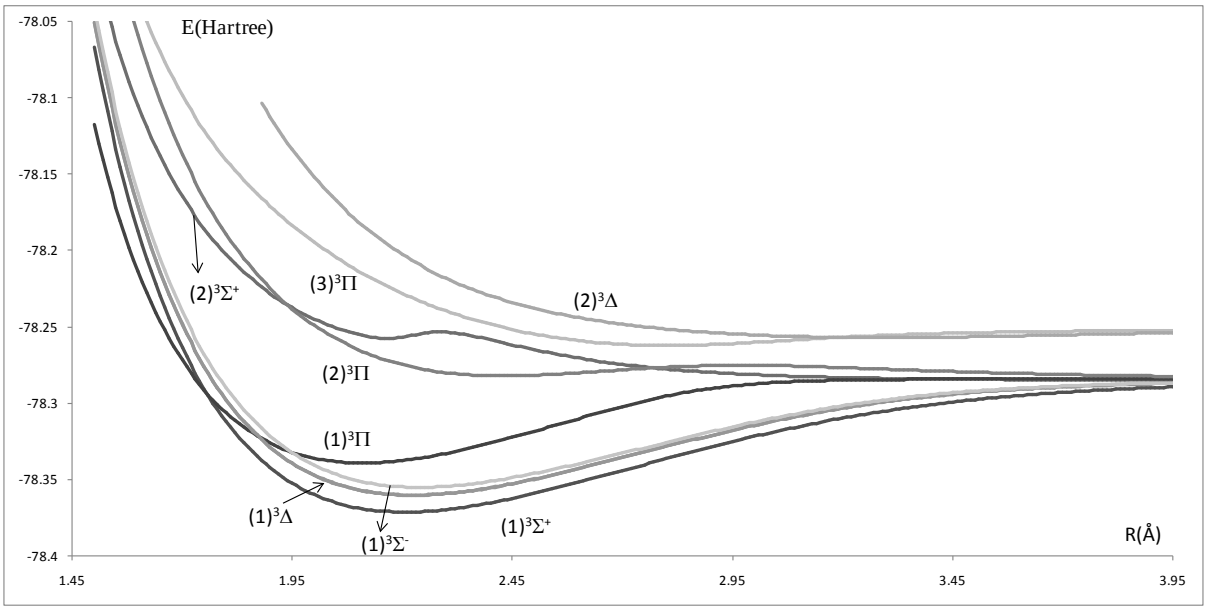
The electric dipole moment is a fundamental electrostatic property, it is useful in finding the strength of the long-range dipole-dipole forces, and the understanding of the macroscopic properties of imperfect gases, liquids and solids. Our MRCI calculation of the DMCs produces smooth and continuous curves even close to the avoided crossings. At large internuclear distances, the dipole moment of all the investigated electronic states smoothly approaches zero which is theoretically the correct behavior for a molecule that dissociates into natural fragments. It is quite common for the molecular electronic states of the potential energy curves to make crossings or avoided crossings known as conical intersections (**Figure 3** and **Figure 4**).

These points of the potential energy curves of a diatomic molecule are important in photochemistry. In fact, the avoided crossing regions are likely to be a leakage channels along which the molecules flow from the higher down to the lower potential energy curves. Such crossings or avoided crossings can dramatically alter the stability of the molecules. If these crossings are overlooked, then low barrier transitions can be missed and an incorrect chemical picture will arise. In the range of R considered, several avoided crossings have been detected in the potential energy curves of the excited electronic states of the molecule PbO.

The dipole moment function of these states exhibits an abrupt change reflecting the avoided crossing between the two states as also observed at the potential energy curves. The agreement between the positions of the avoided crossings of the PECs of the electronic states $(2)^1\Pi$ and $(3)^1\Pi$ (**Figure 1**) and $(2)^3\Pi$ and $(3)^3\Pi$ (**Figure 2**)



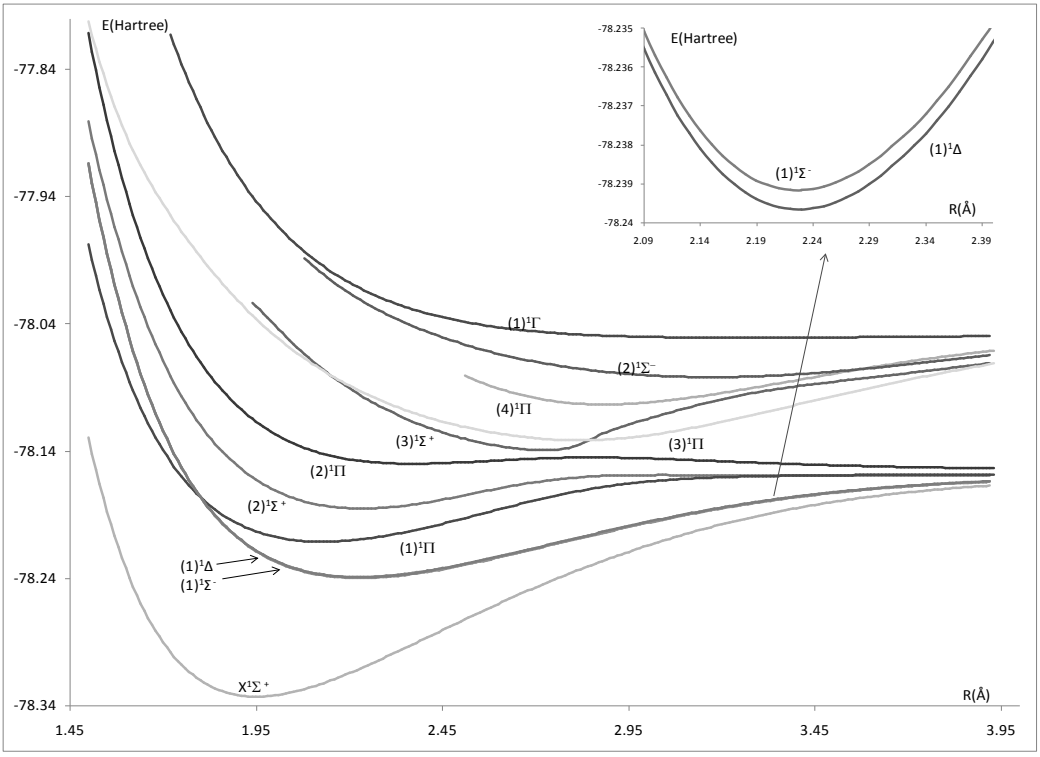
(a)



(b)

Figure 1. Potential energy curves of the lowest electronic states of the molecule PbO using the first basis set: ECP78MWB and 6-311++G** for Pb and O atoms respectively. (a) Singlet electronic states $^1\Sigma^{\pm}$, $^1\Delta$, $^1\Pi$; (b) Triplet electronic states $^3\Sigma^{\pm}$, $^3\Delta$, $^3\Pi$.

with the positions of the crossing of the corresponding DMCs at the points 2.5 Å (**Figure 3**) and 2.8 Å (**Figure 4**) respectively can be considered as confirmation of the accuracy of the present results. In the present calculation of the DMCs we considered the lead atom at the origin. One can notice that, some parts of the DMCs are positive where the lead atom is charged negatively and the other main parts are negative where the charges of the 2



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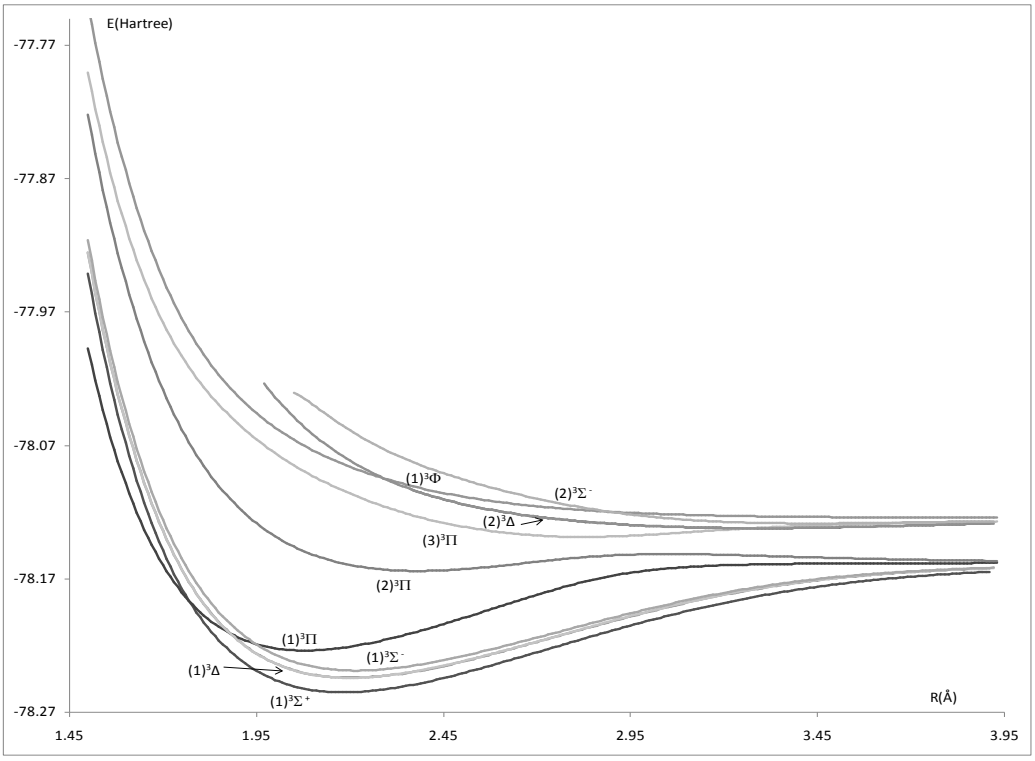
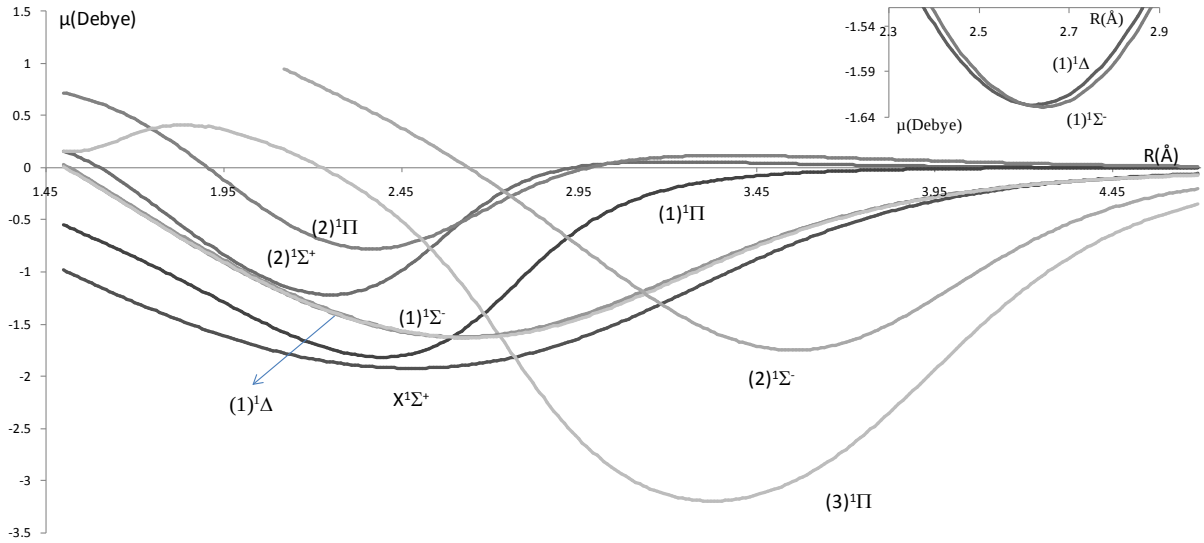


(b)

Figure 2. Potential energy curves of the lowest electronic states of the molecule PbO using the second basis set: ECP78MWB and DGauss-a2-X fit for Pb and O atoms respectively. (a) Singlet electronic states $^1\Sigma^{\pm}$, $^1\Delta$, $^1\Pi$; (b) Triplet electronic states $^3\Sigma^{\pm}$, $^3\Delta$, $^3\Pi$.



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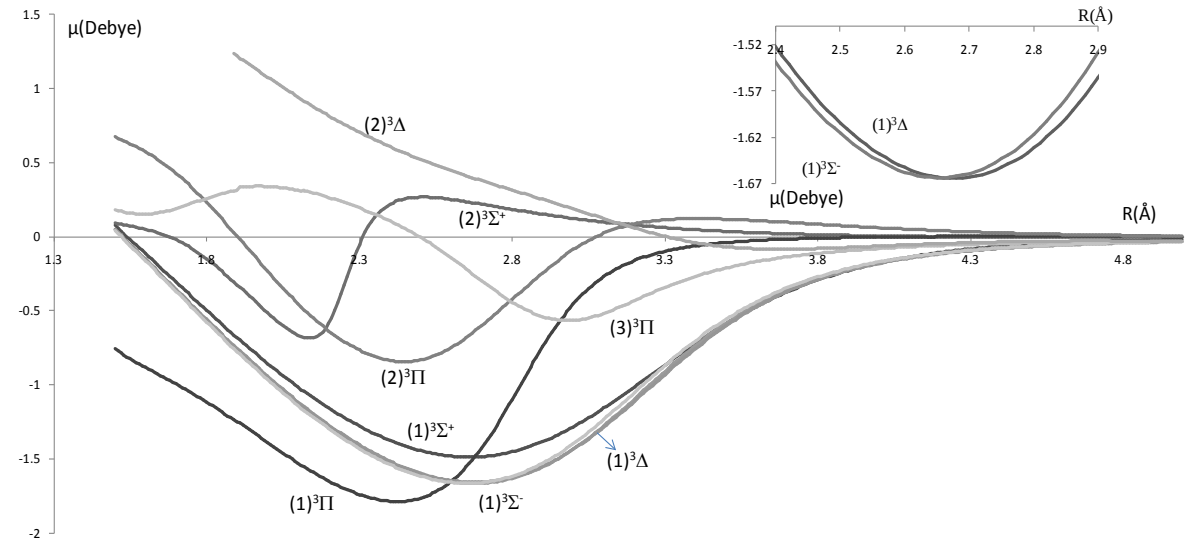
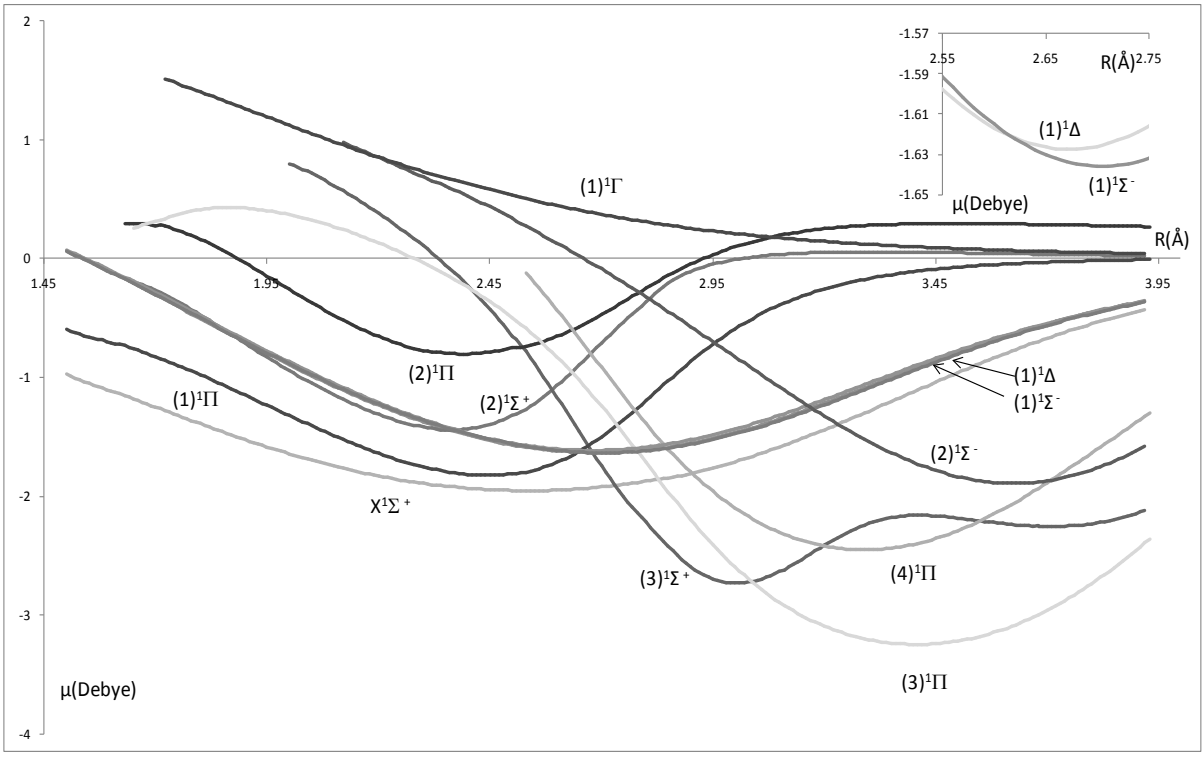


(b)

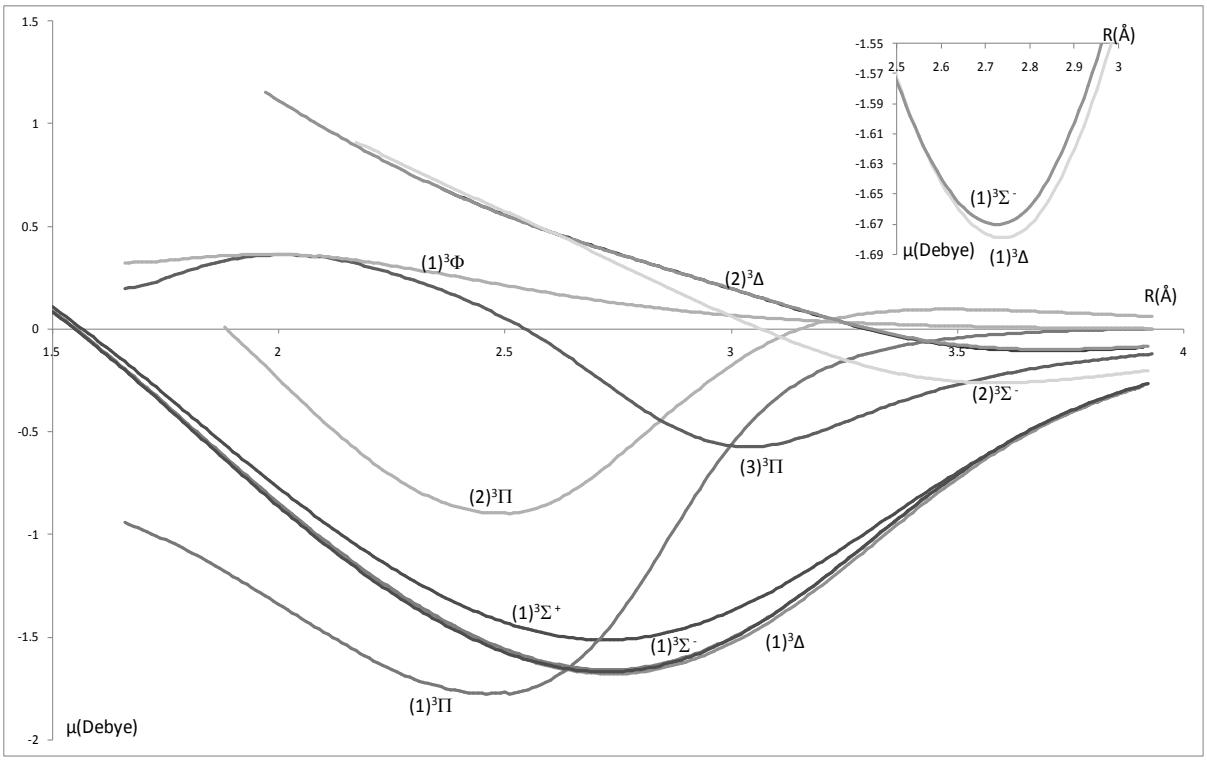
Figure 3. Dipole moment curves of the lowest electronic states of the molecule PbO using the first basis set: ECP78MWB and 6-311++G** for Pb and O atoms respectively. (a) Singlet electronic states $^1\Sigma^{\pm}$, $^1\Delta$, $^1\Pi$; (b) triplet electronic states $^3\Sigma^{\pm}$, $^3\Delta$, $^3\Pi$.

atoms are reversed.

By fitting the calculated energy values around the equilibrium position to a polynomial in terms of the internuclear distance, the spectroscopic constants ω_e, r_e, B_e, and T_e have been calculated by using the PECs obtained by the 2 different ways of calculation. These values are given in **Table 1** along with the available data given in the literature. The comparison of our results with the calculated values for R_e by different techniques in literature for the ground state shows a good agreement with the relative differences 1.3% (Ref. [26]) $\leq \Delta R_e/R_e \leq$ 5.2% (Ref. [5]) and 0.61% (Ref. [26]) $\leq \Delta R_e/R_e \leq$ 4.4% (Ref. [5]) using the first and second way of calculation respectively. For B_e, the comparison of our calculated values with those of Schwenzer *et al.* [5], for the ground state, showed the relative differences 9.8% and 8.4% for the first and the second way respectively, while these relative differences showed the good agreement 3.5% and 2.5% by comparing our values with those of Jalbout *et al.* [26]. For ω_e, the comparison of our results with the fourteen values calculated by different techniques in literature for the ground state show the relative differences 8.6% (Ref. [26]) $\leq \Delta\omega_e/\omega_e \leq$ 28.8% (Ref. [4]) and 4.9% (Ref. [26])



(a)



(b)

Figure 4. Dipole moment curves of the lowest electronic states of the molecule PbO using the second basis set: ECP78MWB and DGauss-a2-X fit for Pb and O atoms respectively. (a) Singlet electronic states $^1\Sigma^{\pm}$, $^1\Delta$, $^1\Pi$; (b) Triplet electronic states $^3\Sigma^{\pm}$, $^3\Delta$, $^3\Pi$.

$\leq \Delta\omega_e/\omega_e \leq 25.9\%$ (Ref. [4]) for the first and second way respectively. This comparison shows that our values for ω_e are in disagreement with those given in Ref. [4], while there is a good agreement for the theoretical values of R_e, B_e and ω_e of Jalbout *et al.* [26] and our calculated values for these constants. The comparison of our calculated values of T_e, using the 2 different ways of calculation, for the two states $(1)^3\Sigma^+$ and $(1)^3\Pi$ with those calculated in literature [9] shows a good agreement with the relative difference $1.6\% \leq \Delta T_e/T_e \leq 7.9\%$.

One can notice that the use of 2 ways of calculation for R_e and T_e have no influence on the calculated values of these constants, but there is an influence on the value of ω_e and large influence on the calculated value of the dipole moment. Moreover our calculated values of dipole moment by using the second way are not in good accuracy with those calculated in literature, while our calculated values by using the first way of calculation are in good agreement with the experimental data of Huber and G. Herzberg [1]. These values are given in **Table 1**. From this over all agreement between our investigated values of the spectroscopic constants and those found in literature, we can pretend the validity of the used technique of calculation and the accuracy of our calculation for the new investigated electronic states. The future experimental investigation for these new electronic states may confirm our results.

Table 1. Spectroscopic constants for the lowest singlet and triplet electronic states of the molecule PbO.

States	T_e (cm^{-1})	$\delta T_e/T_e$ %	ω_e (cm^{-1})	$\delta\omega_e/\omega_e$%	R_e (Å)	$\delta R_e/R_e$ %	B_e (cm^{-1})	$\delta B_e/B_e$ %	μ (a.u)	$\delta\mu/\mu$ %
$X^1\Sigma^+$	0.0		626.9^{0a1} 652.63^{a2}		1.966^{a1} 1.951^{a2}		0.293^{a1} 0.298^{a2}		1.922^{a1} 1.585^{a2}	
			721^{b}	13.0^{a1} 9.4^{a2}	1.922^{b}	2.2^{a1} 1.5^{a2}			1.826^{b}	5.2^{a1} 13.2^{a2}
			718^{c}	12.6^{a1} 9.1^{a2}	1.928^{c}	1.9^{a1} 1.2^{a2}				
			868^{d}	27.7^{a1} 24.8^{a2}	1.868^{d}	5.2^{a1} 4.4^{a2}	0.325^{d}	9.8^{a1} 8.3^{a2}		
			748^{e}	16.18^{a1} 12.7^{a2}	1.915^{e}	2.6^{a1} 1.8^{a2}				
			800^{e}	21.6^{a1} 18.4^{a2}	1.882^{e}	4.4^{a1} 3.6^{a2}				
			881^{e}	28.8^{a1} 25.9^{a2}	1.897^{e}	3.6^{a1} 2.8^{a2}				
			715^{f}	12.3^{a1} 8.7^{a2}	2.020^{f}	2.7^{a1} 3.4^{a2}				
									2.121^{g}	9.3^{a1} 25.2^{a2}
					1.907^{g}	3.1^{a1} 2.3^{a2}			2.2^{g}	12.6^{a1} 27.9^{a2}
									2.203^{g}	12.7^{a1} 28.0^{a2}
			723^{h}	13.1^{a1} 9.7^{a2}	1.926^{h}	2.1^{a1} 1.3^{a2}				
			686.34^{n}	8.6^{a1} 4.9^{a2}	1.939^{n}	1.3^{1a} 0.6^{a2}				
			719.19^{n}	12.8^{a1} 9.2^{a2}	1.918^{n}	2.5^{a1} 1.7^{a2}				
			711.09^{n}	11.8^{a1} 8.2^{a2}	1.922^{n}	2.2^{a1} 1.5^{a2}				
			721.8312^{n}	13.5^{a1} 9.5^{a2}	1.920^{n}	2.3^{a1} 1.6^{a2}	0.308913^{n}	5.1^{a1} 3.5^{a2}		

Continued

			725.5854[n]	13.6[a1] 10.1[a2]	1.93[n]	1.8[a1] 1.1[a2]	0.30572[n]	4.1[a1] 2.5[a2]		
			724.6454[n]	13.4[a1] 9.9[a2]						
									2.263[k]	15.1[a1] 29.9[a2]
									2.2484[k]	14.5[a1] 29.5[a2]
									2.439[l]	21.1[a1] 35.0[a2]
									2.425[l]	20.7[a1] 34.63[a2]
									2.438[l]	21.1[a1] 34.9[a2]
									2.421[l]	20.5[a1] 34.5[a2]
									2.138[m]	10.1[a1] 25.8[a2]
$(1)^3\Sigma^+$	15767.4[a1] 17058.7[a2] 16029[o]	1.6[a1] 6.4[a2]	449.72[a1] 454.63[a2] 478.7[o]	6.4[a1] 5.0[a2]	2.207[a1] 2.182[a2]		0.233[a1] 0.238[a2]		1.17[a1] 1.064[a2]	
$(1)^3\Delta$	18181.7[a1] 19458.7[a2]		441.80[a1] 447.99[a2]		2.222[a1] 2.200[a2]		0.229[a1] 0.234[a2]		1.353[a1] 1.189[a2]	
$(1)^1\Delta$	19247.9[a1] 20470.9[a2]		421.29[a1] 419.06[a2]		2.250[a1] 2.227[a2]		0.224[a1] 0.228[a2]		1.385[a1] 1.293[a2]	
$(1)^1\Sigma^-$	19313.0[a1] 20579.2[a2]		420.04[a1] 419.83[a2]		2.250[a1] 2.226[a2]		0.224[a1] 0.229[a2]		1.379[a1] 1.268[a2]	
$(1)^3\Sigma^-$	19315.9[a1] 20633.0[a2]		431.54[a1] 427.45[a2]		2.237[a1] 2.215[a2]		0.226[a1] 0.231[a2]		1.353[a1] 1.24[a2]	
$(1)^3\Pi$	22826.3[a1] 23945.4[a2] 22175[p]	2.9[a1] 7.9[a2]	468.00[a1] 476.12[a2]		2.111[a1] 2.079[a2]		0.254[a1] 0.262[a2]		1.554[a1] 1.449[a2]	
$(1)^1\Pi$	25581.1[a1] 26707.5[a2]		442.82[a1] 438.19[a2]		2.159[a1] 2.125[a2]		0.243[a1] 0.251[a2]		1.634[a1] 1.536[a2]	
$(2)^1\Sigma^+$	32296.4[a1] 32448.3[a2]		437.78[a1] 442.93[a2]		2.244[a1] 2.231[a2]		0.225[a1] 0.227[a2]		1.217[a1] 1.35[a2]	
$(2)^3\Pi$	35349.4[a1] 37028.3[a2]		306.02[a1] 341.56[a2]		2.431[a1] 2.379[a2]		0.191[a1] 0.200[a2]		0.842[a1] 0.857[a2]	
$(3)^3\Pi$	39719.1[a1] 42633.4[a2]		255.76[a1] 252.86[a2]		2.799[a1] 2.819[a2]		0.144[a1] 0.142[a2]		0.441[a1] 0.439[a2]	
$(2)^1\Pi$	40154.7[a2]		354.54[a2]		2.366[a2]		0.202[a2]		0.798[a2]	
$(2)^3\Sigma^+$	40781.3[a1]		708.26[a1]		2.161[a1]		0.242[a1]		0.66[a1]	
$(2)^3\Delta$	40837.0[a1] 44061.9[a2]		130.84[a1] 134.91[a2]		3.280[a1] 3.287[a2]		0.105[a1] 0.105[a2]		0.007[a1] 0.009[a2]	
$(3)^1\Pi$	42086.7[a1] 44212.0[a2]		352.09[a1] 350.81[a2]		2.769[a1] 2.818[a2]		0.148[a1] 0.1428[a2]		1.824[a1] 1.815[a2]	
$(3)^1\Sigma^+$	42523.3[a2]		510.08[a2]		2.722[a2]		0.153[a2]		1.853[a2]	
$(2)^3\Sigma^-$	44847.4[a2]		129.57[a2]		3.431[a2]		0.963[a2]		0.239[a2]	
$(4)^1\Pi$	50404.3[a2]		402.62[a2]		2.872[a2]		0.137[a2]		1.721[a2]	
$(2)^1\Sigma^-$	52886.3[a1] 55112.9[a2]		217.35[a1] 218.76[a2]		3.130[a1] 3.174[a2]		0.115[a1] 0.112[a2]		1.193[a1] 1.253[a2]	

[a1]Present work using, for the 82 electrons of the Lead atom, a contracted ECP78MWB basis set for s, p, and d functions. While the oxygen species is treated as a system of 8 electrons by using the 6-311++G** basis set for s, p, and d functions. [a2]Present work using, for the 82 electrons of the Lead atom, a contracted ECP78MWB basis set for s, p ,and d functions ,while the oxygen species is treated as a system of 8 electrons by using the DGauss-a2-Xfit basis set for s, p, and d functions. [b]Ref. [1], [c]Ref [12], [d]Ref. [5], [e]Ref [4], [f]Ref. [7], [g]Ref. [3], [h]Ref. [19], [k]Ref. [20], [l]Ref. [21], [m]Ref. [6], [n]Ref. [25], [o]Ref. [9], [p]Ref. [26],

2.2. The Vibration-Rotation Calculation

By using the canonical functions approach [23]-[25] and the cubic spline interpolation between each two consecutive points of the PECs obtained from the *ab initio* calculation of the PbO molecule, the eigenvalue E_v, the rotational constant B_v, and the abscissas of the turning point R_{min} and R_{max} have been calculated for the considered electronic states up to the vibrational levels v = 41. These values for the different electronic states are given in **Table 2**. The absence of the comparison with other results is because of the calculation of these values here for the first time.

Table 2. Values of the eigenvalues E_v, the rotational constants B_v and the abscissas of the turning points for the different vibrational levels of the singlet and triplet electronic states of the molecule PbO.

	$(1)^1\Delta$				$(1)^3\Sigma^-$				$(3)^1\Pi$			
V	E_v (cm^{-1})	B_v (cm^{-1})	R_{min} (Å)	R_{max} (Å)	E_v (cm^{-1})	B_v (cm^{-1})	R_{min} (Å)	R_{max} (Å)	E_v (cm^{-1})	B_v (cm^{-1})	R_{min} (Å)	R_{max} (Å)
0	209.6	0.223	2.18	2.328	214.7	0.225	2.168	2.314	175.6	0.1481	2.689	2.849
1	625.1	0.221	2.133	2.389	640.6	0.224	2.121	2.374	525.5	0.1484	2.630	2.909
2	1037.4	0.22	2.103	2.435	1063.0	0.223	2.091	2.419	871.5	0.1486	2.589	2.952
3	1446.0	0.218	2.079	2.473	1481.8	0.221	2.067	2.457	1213.9	0.1487	2.556	2.987
4	1850.5	0.217	2.059	2.508	1896.6	0.220	2.048	2.491	1553.4	0.1488	2.528	3.018
5	2250.7	0.216	2.042	2.541	2307.5	0.219	2.030	2.522	1889.8	0.14892	2.503	3.047
6	2646.6	0.214	2.027	2.571	2714.5	0.217	2.015	2.552	2223.4	0.1489	2.481	3.074
7	3038.5	0.213	2.013	2.600	3117.8	0.216	2.001	2.581	2554.3	0.1488	2.460	3.100
8	3426.4	0.211	2.000	2.628	3517.3	0.214	1.989	2.608	2882.5	0.1487	2.441	3.123
9	3810.2	0.210	1.989	2.656	3912.8	0.213	1.977	2.634	3208.1	0.1486	2.423	3.148
10	4189.7	0.208	1.978	2.682	4304.4	0.211	1.967	2.660	3531.2	0.1484	2.407	3.171
11	4565.0	0.207	1.968	2.708	4692.2	0.210	1.957	2.686	3851.8	0.1483	2.391	3.193
12	4936.0	0.205	1.959	2.734	5076.0	0.209	1.947	2.710	4170.0	0.1480	2.376	3.215
13	5302.9	0.204	1.95	2.760	5455.9	0.207	1.939	2.735	4485.7	0.1470	2.362	3.237
14	5665.2	0.202	1.942	2.785	5831.7	0.206	1.930	2.759	4799.0	0.1475	2.348	3.258
15	6023.2	0.201	1.934	2.810	6203.5	0.204	1.922	2.783	5109.9	0.1472	2.336	3.279
16	6376.9	0.199	1.926	2.835	6571.2	0.203	1.915	2.807	5418.4	0.1469	2.323	3.300
17	6726.0	0.197	1.919	2.860	6934.8	0.201	1.908	2.831	5724.6	0.1465	2.311	3.321
18	7070.6	0.196	1.912	2.884	7294.1	0.200	1.901	2.854	6028.4	0.1462	2.300	3.341
19	7410.6	0.194	1.906	2.909	7649.1	0.198	1.895	2.878	6329.8	0.1458	2.289	3.362
20	7745.9	0.192	1.900	2.934	7999.8	0.197	1.888	2.902	6628.9	0.1454	2.279	3.382
21	8076.1	0.191	1.894	2.959	8345.9	0.195	1.882	2.926	6925.7	0.1449	2.269	3.402
22	8401.6	0.189	1.889	2.985	8687.4	0.193	1.877	2.950	7220.0	0.1445	2.259	3.422
23	8722.2	0.187	1.883	3.011	9024.1	0.192	1.871	2.974	7512.0	0.1440	2.250	3.442
24	9037.5	0.185	1.878	3.036	9355.9	0.190	1.866	2.998	7801.6	0.1435	2.240	3.462
25	9347.5	0.183	1.873	3.062	9682.6	0.188	1.861	3.023	8088.9	0.1430	2.232	3.482
26	9652.2	0.182	1.868	3.089	10003.9	0.186	1.856	3.048	8373.7	0.1425	2.223	3.502
27	9951.4	0.180	1.864	3.116	10319.8	0.185	1.851	3.073	8656.2	0.1420	2.215	3.523
28	10244.8	0.178	1.859	3.143	10630.0	0.183	1.847	3.099	8936.3	0.1414	2.207	3.543
29	10532.5	0.176	1.855	3.171	10934.4	0.181	1.842	3.125	9213.9	0.1409	2.199	3.563

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30	10814.1	0.174	1.851	3.199	11232.6	0.179	1.838	3.152	9489.0	0.1403	2.191	3.583
31	11089.8	0.172	1.847	3.229	11524.5	0.176	1.834	3.180	9761.7	0.1397	2.184	3.604
32	11359.1	0.169	1.843	3.259	11809.7	0.174	1.830	3.209	10031.9	0.1390	2.177	3.624
33	11622.0	0.167	1.840	3.289	12087.9	0.172	1.827	3.239	10299.6	0.1384	2.170	3.645
34	11878.6	0.165	1.836	3.320	12358.7	0.169	1.823	3.269	10564.6	0.1377	2.163	3.665
35	12128.2	0.162	1.833	3.353	12621.8	0.166	1.820	3.302	10827.1	0.1370	2.156	3.686
36	12371.1	0.160	1.830	3.387	12876.6	0.164	1.817	3.335				
37	12606.7	0.157	1.827	3.422	13122.9	0.161	1.814	3.371				
38	12835.2	0.154	1.824	3.458	13360.0	0.158	1.811	3.408				
39	13056.2	0.152	1.821	3.496	13587.4	0.154	1.808	3.448				
40	13269.3	0.149	1.818	3.535	13804.7	0.151	1.806	3.495				
41	13474.4	0.146	1.816	3.576								
		$(1)^1\Pi$				$(1)^3\Delta$				$(1)^3\Sigma^+$		
0	220.5	0.242	2.09	2.234	214.8	0.228	2.154	2.299	81.9	0.231	2.097	2.333
1	658.3	0.241	2.043	2.293	641.2	0.227	2.107	2.360	243.3	0.227	2.027	2.439
2	1092.7	0.240	2.013	2.337	1063.8	0.226	2.076	2.404	401.2	0.223	1.983	2.520
3	1523.3	0.238	1.989	2.374	1482.8	0.224	2.053	2.442	555.4	0.220	1.950	2.591
4	1949.3	0.237	1.970	2.407	1898.0	0.223	2.033	2.476	705.7	0.216	1.923	2.658
5	2371.2	0.235	1.953	2.438	2309.4	0.221	2.016	2.507	852.1	0.212	1.900	2.722
6	2788.4	0.234	1.937	2.468	2716.9	0.220	2.000	2.537	994.4	0.208	1.880	2.784
7	3200.7	0.232	1.924	2.496	3120.6	0.219	1.987	2.566	1132.7	0.204	1.862	2.845
8	3607.9	0.230	1.911	2.524	3520.4	0.217	1.974	2.593	1266.6	0.200	1.847	2.906
9	4009.7	0.229	1.900	2.551	3916.4	0.216	1.963	2.619	1396.2	0.195	1.833	2.968
10	4405.6	0.227	1.889	2.578	4308.4	0.214	1.952	2.645	1521.1	0.191	1.820	3.031
11	4795.3	0.225	1.879	2.604	4696.5	0.213	1.942	2.670	1641.1	0.186	1.809	3.096
12	5178.5	0.223	1.870	2.631	5080.8	0.211	1.933	2.695	1756.0	0.181	1.798	3.163
13	5554.4	0.221	1.862	2.658	5461.0	0.210	1.924	2.720	1865.3	0.176	1.789	3.234
14	5922.6	0.218	1.854	2.686	5837.3	0.208	1.916	2.744	1968.7	0.170	1.780	3.310
15	6282.4	0.216	1.846	2.714	6209.5	0.207	1.908	2.768				
16	6632.6	0.213	1.839	2.744	6577.7	0.205	1.900	2.792				
17	6972.2	0.210	1.833	2.774	6941.8	0.204	1.893	2.816				
18	7299.8	0.206	1.827	2.807	7301.8	0.202	1.886	2.839				
19	7613.8	0.202	1.821	2.842	7657.5	0.201	1.880	2.863				
20	7912.1	0.198	1.816	2.881	8009.0	0.199	1.874	2.886				
21	8192.5	0.192	1.811	2.925	8356.1	0.198	1.868	2.910				
22	8451.9	0.186	1.807	2.975	8698.7	0.196	1.862	2.934				
23	8686.5	0.178	1.803	3.035	9036.8	0.194	1.857	2.957				
24	8891.9	0.168	1.799	3.110								
25	9061.9	0.155	1.797	3.211								

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	$(3)^3\Pi$				$(2)^1\Sigma^+$				$(2)^3\Pi$			
0	126.6	0.144	2.71	2.899	216.2	0.223	2.176	2.321	150.9	0.19	2.351	2.525
1	375.1	0.143	2.649	2.981	638.4	0.221	2.132	2.387	444.9	0.188	2.299	2.605
2	614.6	0.141	2.61	3.046	1044.7	0.218	2.104	2.439	726.2	0.184	2.267	2.669
3	843.6	0.139	2.579	3.105	1433.1	0.214	2.083	2.486	991.6	0.181	2.243	2.731
4	1060.3	0.137	2.554	3.165	1800.8	0.211	2.065	2.534				
5	1262.8	0.134	2.533	3.227	2143.5	0.206	2.051	2.584				
6	1449.8	0.131	2.516	3.295	2454.3	0.199	2.039	2.642				
7	1619.3	0.127	2.501	3.371								
	$X^1\Sigma^+$				$(1)^3\Pi$							
0	312.000	0.292	1.908	2.029	233.600	0.253	2.044	2.183				
1	928.700	0.291	1.869	2.08	698.000	0.252	1.998	2.241				
2	1540.50	0.289	1.843	2.116	1158.30	0.251	1.969	2.283				
3	2146.20	0.287	1.824	2.147	1615.60	0.249	1.945	2.318				
4	2747.30	0.286	1.807	2.175	2068.70	0.248	1.926	2.350				
5	3344.60	0.284	1.793	2.201	2519.60	0.246	1.910	2.380				
6	3936.90	0.282	1.780	2.225	2966.60	0.245	1.896	2.408				
7	4524.20	0.281	1.768	2.248	3411.00	0.243	1.883	2.435				
8	5107.40	0.279	1.758	2.27	3852.00	0.242	1.870	2.460				
9	5685.90	0.278	1.748	2.292	4288.80	0.240	1.859	2.485				
10	6259.50	0.276	1.739	2.313	4721.60	0.239	1.849	2.509				
11	6828.60	0.274	1.731	2.333	5149.50	0.237	1.839	2.533				
12	7393.20	0.273	1.723	2.353	5573.10	0.236	1.830	2.556				
13	7952.90	0.271	1.716	2.373	5992.80	0.234	1.822	2.579				
14	8507.90	0.269	1.709	2.392	6408.20	0.232	1.813	2.602				
15	9058.30	0.267	1.702	2.411	6819.20	0.231	1.806	2.625				
16	9603.90	0.266	1.696	2.43	7225.00	0.229	1.799	2.648				
17	10144.7	0.264	1.690	2.448	7624.90	0.227	1.792	2.671				
18	10680.7	0.262	1.684	2.467	8018.80	0.225	1.785	2.694				
19	11212.0	0.261	1.678	2.485	8406.70	0.223	1.779	2.718				
20	11738.4	0.259	1.673	2.504	8787.50	0.221	1.773	2.742				
21	12260.0	0.257	1.668	2.522	9160.60	0.218	1.768	2.768				
22	12776.8	0.256	1.663	2.54	9524.80	0.215	1.763	2.794				
23	13288.8	0.254	1.659	2.558	9878.70	0.212	1.758	2.822				
24	13795.8	0.252	1.654	2.576	10220.8	0.209	1.753	2.851				
25	14297.9	0.251	1.650	2.594	10549.4	0.205	1.748	2.884				
26	14795.3	0.249	1.646	2.612	10862.0	0.200	1.744	2.920				
27	15287.7	0.247	1.642	2.63	11154.8	0.194	1.741	2.962				
28	15775.2	0.245	1.638	2.648	11423.2	0.186	1.737	3.013				
29	16257.8	0.244	1.634	2.666	11660.7	0.176	1.734	3.078				
30	16735.5	0.242	1.630	2.684	11857.8	0.161	1.732	3.170				

3. Conclusion

In the present work, the *ab initio* investigation for the low-lying singlet and triplet electronic states of the PbO molecule has been performed via CASSCF/MRCI method using 2 different basis sets. The potential energy and the dipole moment curves have been determined along with the spectroscopic constants T_e, R_e, ω_e and the rotational constant B_e for these electronic states. The comparison of our results with those obtained theoretically in literature showed an overall good accuracy. By using the canonical functions approach [23]-[25], the eigenvalue E_v, the rotational constant B_v, and the abscissas of the turning points $R_{\min}$ and $R_{\max}$ were calculated up to the vibrational level $v = 41$. New electronic states have been investigated in the present work for the first time (nine new for first basis and fourteen new for second basis).

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