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Theoretical study of the spectroscopic constant and anharmonic force field of PO_2^-

Pengfei Wang, Chonghai Qi, Meishan Wang[*], Chuanlu Yang, and Jing Li

School of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, People's Republic of China

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Abstract. The equilibrium structure, spectroscopy constants and anharmonic force field of PO_2^- anion have been investigated at MP2, B3LYP, B3P86, B3PW91 methods employing three basis sets, 6-311++G(2d,2p), 6-311++G(3df,3pd) and cc-pVQZ, respectively. The computed geometries, rotational constants, vibration-rotation interaction constants, quartic centrifugal distortion constants, and coriolis coupling constants of PO_2^- are compared with the available experimental or theoretical data. The fundamental frequencies, rotational constants of ground state, sextic centrifugal distortion constants, cubic and quartic force constants of PO_2^- are firstly predicted. The calculated results show that the B3P86/6-311++G(3df, 3pd) results are in excellent agreement with experiment and represent a substantial improvement over the results obtained from MP2. The other DFT methods are also advisable choices to study the anharmonic force field of PO_2^-. The predicted spectroscopic constants may provide the useful data for the experiment studies of the corresponding spectroscopic constants of PO_2^-.

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Key words: PO_2^- anion; *ab initio* calculations; spectroscopic constants; anharmonic force field.

1 Introduction

The oxidation of phosphorus has received an increasing interest over centuries. In order to satisfy the need of destroying chemical warfare agents, involving organophosphorus agents, a good understanding about the combustion of organophosphorus compounds appears to be of great importance [1-3]. What is more, the phosphorus-oxygen chemistry is quite complicated due to the abound species formed in the phosphorus-oxidation. As

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[*]Corresponding author. *Email address:* `mswang1971@163.com` (M.-S. Wang)

far as we know, both PO_2 free radical and PO_2^- anion are two major reactants occurring in oxidations of phosphorous compounds [1-5].

The PO_2 radical is a key intermediate in phosphorus combustion chemistry. In order to study the spectroscopic properties of PO_2, the microwave, electronic absorption, far infrared laser magnetic resonance and diode laser absorption spectroscopies were observed [6-10]. Meanwhile, a series of high-level *ab initio* calculation of PO_2 were finished [11-16] and the spectroscopic constants of PO_2, such as the equilibrium geometries, vibrational frequencies, and force constants were obtained.

Considerably PO_2^- anion is also one of the possible anionic species occurring in oxidations of phosphorus compounds [13, 15, 17-20]. In 1979, Hunter *et al.* [17] performed the optical and vibrational spectra of PO_2^- anion trapped substitutionally in alkali halide lattices and obtained the vibrtional frequencies ω_1=1097cm^{-1}, ω_2=501cm^{-1} and ω_3=1207cm^{-1}, which was used to calculate the P-O bond length r_{PO}=1.65 Å and the OPO angle θ_{OPO}=110°. However, the above calculation was considered to be incomplete. Five years later, the geometries and vibrational frequencies of PO_2^- were calculated at the level of HF/6-31G* by Lohr *et al.* [11]. In 1995, Xu *et al.* [13] reported the first gas phase experiment for PO_2^- and determined the geometric parameters: r_{PO}=1.50±0.01 Å, θ_{OPO}=120.0±0.1° using the FG matrix method. In addition, the geometries and vibrational frequencies on the X^1A_1 state of PO_2^- were calculated at MP2 level. In 1996, Pak *et al.* [18] carried out the spectroscopic parameters including the equilibrium geometries, rotational constants, vibration-rotation interaction constants, quartic centrifugal distortion constants, and so on at the CCSD(T)/ cc-pVQZ level. In 2002, Francisco *et al.* [15] investigated the geometric parameters, rotational constants and vibrational frequencies using the CCSD(T) method with cc-pvNz(N=D, T, Q) and aug-cc-pvNz(N=D, T, Q) basis sets. In 2008, Zhang *et al.* [19] gave the geometry optimization and harmonic vibrational frequency calculations on the X^1A_1 state of PO_2^-. The equilibrium geometry parameters, r_{PO}=1.504±0.005 Å and θ_{OPO}=119.0±0.2° on the X^1A_1 state of PO_2^- are derived by employing an iterative Franck-Condon analysis procedure. In 2013, Liang *et al.* [20] developed the three-dimensional Franck-Condon overlap integrals to produce a more accurate calculation of the equilibrium structure and harmonic vibrational frequencies on the X^1A_1 state of PO_2^-. They took into account the mode mixing and hot band effects which were ignored by Zhang *et al.*[19]. The equilibrium geometry parameters, r_{PO}=1.495±0.005 Å and θ_{OPO}=119.5±0.5° on the X^1A_1 state of PO_2^- were derived. In conclusion, the force constants, the sextic centrifugal distortion constants and the rotational constants of the ground state are absent in all the previous calculations and the experiment, yet they are necessary to accurately calculate the rovibrational spectra of molecules. On the other hand, the *ab initio* methods have been quite successful and accurate in calculating the spectroscopic constants and anharmonic force field for other AB_2 type molecules [21-23], and it is reasonably confident in their use to calculate the corresponding results for PO_2^-.

In this work, the spectroscopic constants and the anharmonic force field of PO_2^- are performed using MP2, B3LYP, B3P86 and B3PW91 methods with 6-311++G(2d, 2p), 6-311++G(3df,3pd) and cc-pVQZ basis sets, respectively. We investigate the geometry constants, rotational constants, vibration-rotation interaction constants, quartic and sextic centrifugal distortion constants, anharmonic constants, harmonic and fundamental frequencies, coriolis coupling constants, third-order and fourth-order force constants of PO_2^-. In addition, they are compared with the available experimental or previous theoretical data. The paper is organized as follows: In Section 2 we briefly describe the computational methods. The results and discussion are given in Section 3. Finally, the conclusions are summarized in Section 4.

2 Computational methods

Quantum-chemical calculations are carried out at the correlated levels of second-order MØller-plesset perturbation theory (MP2) [24] and density functional methods (B3LYP [25, 26-27], B3P86 [25, 28], B3PW91 [25, 29]). All the calculations are performed with the GAUSSIAN03 program [30]. There are three basis sets are employed in the present work: the first basis set is the correlation consistent polarized valence quadruple-zeta basis (cc-pVQZ [31]). The basis of O is [5s4p3d2f1g] contraction of a [12s6p3d2f1g] primitive set. The basis of P is the [6s5p3d2f1g] contraction of a [16s11p3d2f1g] primitive set. The second basis set is 6-311++G(2d,2p) which corresponds to a [5s4p2d/7s6p2d] contraction of a [12s6p2d/14s10p2d] primitive set for O/P. The third basis set is 6-311++G(3df,3pd) corresponding to a [5s4p3d1f/7s6p3d1f] contraction of a [12s6p3d1f/ 14s10p3d1f] primitive set for O/P.

Spherical harmonics are used throughout. Unless stated otherwise, all elections are correlated. The geometry of PO_2^- is optimized within the constraint of C_{2v} point group symmetry, which can be found in Fig. 1. The anharmonic force fields are calculated at all the levels. The optimized geometry was firstly calculated. Then, the associated harmonic force field was evaluated analytically in Cartesian coordinates at the optimized geometry. The cubic and semi-diagonal quartic normal coordinate force constants are determined with the use of a finite difference procedure involving displacements along the reduced normal coordinates and the analytic second derivatives are calculated at these displaced geometries. The anharmonic spectroscopic constants were derived from the theoretical normal coordinate force fields applying the standard formulas based on second-order rovibrational perturbation theory [32, 33].

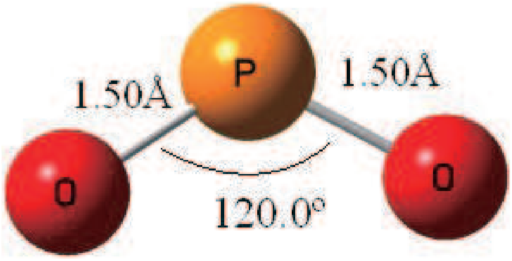

Figure 1: The geometrical parameters of PO_2^- anion.

3 Result and discussions

The calculated results of the molecular geometries, the spectroscopic constants, and the full quartic force fields of PO_2^- using MP2, B3LYP, B3P86, B3PW91 methods are given in Tables 1-8. They are compared with the corresponding experimental [13, 17] or calculated data [13, 15, 18, 19] whenever these are available.

The calculated and experimentally derived equilibrium structures of the X^1A_1 state of PO_2^- are listed in Table 1. The OP bond length of PO_2^- is overestimated by MP2 about 0.0108-0.0194 Å, while the DFT methods with the basis of cc-pVQZ and 6-311++G(3df, 3pd) reproduce the experimental values to within 0.0077 Å (with slightly larger deviation for the 6-311++G(2d,2p) basis, up to 0.0109 Å). The angle ∠OPO of PO_2^- is underestimated by almost all theoretical levels. It is also obvious that the theoretical value of the angle ∠OPO increases in the range of cc-pVQZ, 6-311++G(2d,2p) and 6-311++G(3df,3pd). This indicates that the addition of a f-polarized and diffuse functions produces a substantial improvement in the geometry structure. Within the experimental uncertainty, The B3P86/6-311++G(3df, 3pd) level provides the best overall agreement between theory and experiment results.

Table 1: The geometrical parameters and harmonic and fundamental frequencies of PO_2^-(cm^{-1}).

Method	r_{OP}(Å)	θ_{OPO}(°)	ω_1	ω_2	ω_3	v_1	v_2	v_3
MP2/6-311++G(3df,3pd)	1.5108	120.0022	1035.532	442.390	1196.868	1023.547	438.722	1181.434
Mp2/6-311++G(2d,2p)	1.5194	119.9039	1011.887	442.143	1168.381	999.918	438.433	1152.894
MP2/cc-pVQZ	1.5125	119.2495	1048.259	452.167	1208.473	1036.507	448.818	1193.732
B3LYP/6-311++G(3df,3pd)	1.5039	119.3479	1060.025	453.959	1211.577	1047.640	450.588	1194.897
B3LYP/6-311++G(2d,2p)	1.5109	119.1787	1042.256	448.954	1187.235	1029.595	445.620	1170.271
B3LYP/ cc-pVQZ	1.5077	118.5186	1064.870	461.805	1210.202	1052.761	458.693	119.321
B3P86/6-311++G(3df,3pd)	1.4994	119.2307	1075.756	457.610	1230.156	1064.065	454.387	1214.520
B3P86/6-311++G(2d,2p)	1.508	119.0306	1059.613	453.169	1207.507	1047.558	449.983	1191.468
B3P86/ cc-pVQZ	1.5033	118.4848	1079.349	464.350	1227.680	1067.858	461.416	1212.720
B3PW91/6-311++G(3df,3pd)	1.5012	119.2493	1070.759	456.793	1224.651	1059.206	453.544	1209.190
B3PW91/6-311++G(2d,2p)	1.508	119.0811	1053.897	452.168	1201.316	1042.066	449.045	1185.638
B3PW91/ cc-pVQZ	1.5052	118.4747	1074.516	464.050	1221.897	1063.213	461.119	1207.206
Ref.[13][a]	1.5048	119.381	1135.1	497.5	1303.0			
Ref.[18][b]	1.5063	118.86	1071.9	463.6	1227.9	1059.6	460.3	1212.6
Ref.[19][c]	1.5193	119.8453	1012.5	442.3	1168.7			
Ref.[19][d]	1.5038	119.4375	1075.4	467.8	1225.8			
Ref.[19][e]	1.5108	119.1474	1042.6	449.1	1187.4			
Exp.[13]	1.500.01	120.00.1	1000	470	-			
Exp.[17]	1.65	110	1097	501	1207			

[a] CISD/6-31G*.

[b] CCSD(T)/cc-pVQZ.

[c] MP2/6-311+G(2d,p).

[d] CCSD/6-311+G(2d,p).

[e] B3LYP/6-311+G(2d,p).

Table 2: Rotational constants of equilibrium and ground states of PO_2^- (cm^{-1}).

Method	A_e	B_e	C_e	A_0	B_0	C_0
MP2/6-311++G(3df,3pd)	1.8774446	0.3078302	0.2644675	1.8898849	0.3066514	0.2631818
MP2/6-311++G(2d,2p)	1.8507364	0.3046557	0.2615939	1.8619404	0.3034744	0.2602962
MP2/cc-pVQZ	1.8312768	0.3094753	0.2647364	1.8427354	0.3082960	0.2634639
B3LYP/6-311++G(3df,3pd)	1.8578296	0.3127278	0.2676709	1.8687831	0.3116411	0.2664388
B3LYP/6-311++G(2d,2p)	1.8313741	0.3103687	0.2653919	1.8423859	0.3092243	0.2641270
B3LYP/ cc-pVQZ	1.8036642	0.3138212	0.2673114	1.8137144	0.3127073	0.2660733
B3P86/6-311++G(3df,3pd)	1.8623945	0.3149710	0.2694082	1.8734640	0.3139093	0.2681976
B3P86/6-311++G(2d,2p)	1.8352491	0.3128709	0.2673017	1.8462441	0.3117646	0.2660658
B3P86/ cc-pVQZ	1.8125065	0.3157835	0.2689293	1.8227535	0.3146971	0.2677132
B3PW91/6-311++G(3df,3pd)	1.8589043	0.3141469	0.2687323	1.8699947	0.3130743	0.2675155
B3PW/6-311++G(2d,2p)	1.8330505	0.3118671	0.2665222	1.8441183	0.3107503	0.2652810
B3PW91/ cc-pVQZ	1.8073910	0.3150186	0.2682619	1.8176186	0.3139228	0.2670411
Ref.[18][a]	1.8250287	0.3132800	0.2673816			
Ref.[15][b]	1.8272302	0.3121492	0.2666177			

[a] CCSD(T)/ cc-pVQZ.

[b] CCSD(T)/aug-cc-pVQZ.

Table 1 also includes the calculated harmonic and fundamental vibrational frequencies of PO_2^-. The theoretical fundamental frequencies are derived from the corresponding harmonic frequencies and anharmonic constants. For comparison, the corresponding experimental harmonic frequencies are also listed whenever available, whereas the fundamental frequencies of PO_2^- have not yet been deduced experimentally up to now. As expected, the MP2 results underestimated the harmonic frequencies. The DFT results are much closer to the experiment results. For the symmetric stretching frequency ω_1, the result of DFT method is within $1042\mathrm{cm}^{-1} \sim 1079\mathrm{cm}^{-1}$. Therefore, we think the result from Ref. [17] is more reliable than the one from Ref. [13]. However, for the bending frequency ω_2, we think the result from Ref. [13] is more reliable than the one from Ref. [17]. The three calculated harmonic frequencies by the B3P86/cc-pVQZ level are reproduced within the relative error 1.7%, the relative error is within 2.6% for B3P86/6-311++G(3df, 3pd) level. It can be seen from Table 1 that the B3P86/cc-pVQZ and B3P86/6-311++G(3df, 3pd) levels are well reproduced the geometrical parameters and harmonic frequencies of PO_2^- anion. Besides, they provide the good theoretical prediction for the fundamental frequencies of PO_2^-.

The rotational constants of equilibrium and ground states of the PO_2^- anion are shown in the Table 2. The theoretical ground state rotational constants(A_0, B_0, C_0) are obtained from the associated equilibrium constants (A_e, B_e, C_e) by considering the effects of vibration-rotation coupling via the perturbation theory[32,33]. The experimental rotational constants of equilibrium and ground states of PO_2^- have not been reported so far, the previous calculated equilibrium results were given by CCSD(T)/ cc-pVQZ and CCSD(T)/aug-cc-pVQZ levels[15,18]. One can find from Table 2 that the B3P86/cc-pVQZ results are much closer to the corresponding CCSD(T)/aug-cc-pVQZ ones. Therefore, the calculated rotational constants of ground state of the PO_2^- by the B3P86/cc-pVQZ level can be

Table 3: Vibration-rotation interaction constants of PO_2^-(cm^{-1}).

Method	α_1^A	α_2^A	α_3^A	α_1^B	α_2^B	α_3^B	α_1^C	α_2^C	α_3^C
MP2/6-311++G(3df,3pd)	-0.00520	-0.03952	0.01984	0.00155	-0.00017	0.00097	0.00127	0.00047	0.00090
MP2/6-311++G(2d,2p)	-0.00491	-0.03656	0.01906	0.00156	-0.00023	0.00103	0.00129	0.00039	0.00092
MP2/cc-pVQZ	-0.00472	-0.03589	0.01769	0.00154	-0.00016	0.00098	0.00127	0.00042	0.00086
B3LYP/6-311++G(3df,3pd)	-0.00474	-0.03707	0.01991	0.00150	-0.00021	0.00089	0.00124	0.00039	0.00084
B3LYP/6-311++G(2d,2p)	-0.00497	-0.03604	0.01898	0.00154	-0.00021	0.00096	0.00127	0.00040	0.00086
B3LYP/ cc-pVQZ	-0.00424	-0.03368	0.01782	0.00150	-0.00019	0.00092	0.00125	0.00041	0.00081
B3P86/6-311++G(3df,3pd)	-0.00493	-0.03683	0.01962	0.00149	-0.00023	0.00086	0.00122	0.00038	0.00081
B3P86/6-311++G(2d,2p)	-0.00508	-0.03566	0.01875	0.00152	-0.00022	0.00092	0.00125	0.00039	0.00083
B3P86/ cc-pVQZ	-0.00448	-0.03376	0.01774	0.00149	-0.00020	0.00089	0.00124	0.00040	0.00079
B3PW91/6-311++G(3df,3pd)	-0.00495	-0.03670	0.01947	0.00149	-0.00022	0.00088	0.00122	0.00039	0.00082
B3PW91/6-311++G(2d,2p)	-0.00515	-0.03558	0.01859	0.00152	-0.00022	0.00094	0.00125	0.00039	0.00084
B3PW91/ cc-pVQZ	-0.00450	-0.03347	0.01752	0.00149	-0.00020	0.00091	0.00124	0.00041	0.00080
Ref.[18][a]	-0.00409	-0.03541	0.01797	0.00151	-0.00012	0.00094	0.00126	0.00043	0.00084

[a] CCSD(T)/cc-pVQZ.

Table 4: Anharmonic constants of PO_2^-(cm^{-1}).

Method	X_{11}	X_{12}	X_{13}	X_{22}	X_{23}	X_{33}
MP2/6-311++G(3df,3pd)	-2.82912	-2.292550	-10.3626	-0.553951	-2.82743	-4.41918
MP2/6-311++G(2d,2p)	-2.82988	-2.24852	-10.3704	-0.566632	-2.90489	-4.42460
MP2/cc-pVQZ	-2.79969	-2.34649	-9.95823	-0.358816	-2.91389	-4.15154
B3LYP/6-311++G(3df,3pd)	-2.81826	-2.21106	-11.2862	-0.389511	-2.97443	-4.77509
B3LYP/6-311++G(2d,2p)	-2.86905	-2.26811	-11.5775	-0.342732	-3.02768	-4.83049
B3LYP/ cc-pVQZ	-2.76731	-2.30525	-10.8425	-0.214426	-3.06209	-4.46425
B3P86/6-311++G(3df,3pd)	-2.69158	-2.11987	-10.4947	-0.372127	-2.83832	-4.48499
B3P86/6-311++G(2d,2p)	-2.76395	-2.16888	-10.8862	-0.326716	-2.89468	-4.57458
B3P86/ cc-pVQZ	-2.66111	-2.16948	-10.1690	-0.206213	-2.87435	-4.21908
B3PW91/6-311++G(3df,3pd)	-2.65821	-2.11757	-10.3568	-0.384247	-2.84442	-4.43008
B3PW91/6-311++G(2d,2p)	-2.72332	-2.11113	-10.6574	-0.325840	-2.83175	-4.46666
B3PW91/ cc-pVQZ	-2.61865	-2.15052	-9.98004	-0.210761	-2.86922	-4.13341
Ref.[18][a]	-2.89	-2.48	-10.52	-0.26	-3.07	-4.26

[a] CCSD(T)/cc-pVQZ.

treated as the predicted values.

Theoretical results of the vibration-rotation interaction constants α_i^X(X=A, B, C; i=1-3) of PO_2^- are collected in Table 3. These constants can be used to calculate the ground state rotational constants. So far there are no experimental results on these constants. The only previous theoretical research was finished at the CCSD(T)/cc-pVQZ levels[18]. Comparing with the CCSD(T)/ cc-pVQZ levels, it is easy to find that the calculated vibration-rotation interaction constants by our theory levels have the correct sign and reasonable magnitude, which indicates that the methods and basis sets chosen by us are appropriate for PO_2^-.

Table 4 gives the calculated anharmonic constants (X_{ij}) of the PO_2^- anion. The experimental anharmonic constants of PO_2^- have not been reported to date. The previous

Table 5: Equilibrium quartic centrifugal distortion constants of PO_2^-(cm^{-1}).

Method	$\Delta_J \times 10^4$	$\Delta_{JK} \times 10^4$	$\Delta_K \times 10^4$	$\delta_J \times 10^4$	$\delta_K \times 10^4$
MP2/6-311++G(3df,3pd)	0.00209	-0.04183	0.91886	0.00054	0.00753
Mp2/6-311++G(2d,2p)	0.00208	-0.03956	0.87830	0.00053	0.00752
MP2/cc-pVQZ	0.00209	-0.03889	0.80366	0.00054	0.00728
B3LYP/6-311++G(3df,3pd)	0.00209	-0.03967	0.84448	0.00055	0.00739
B3LYP/6-311++G(2d,2p)	0.00211	-0.03918	0.82140	0.00055	0.00746
B3LYP/ cc-pVQZ	0.00209	-0.03667	0.73550	0.00055	0.00720
B3P86/6-311++G(3df,3pd)	0.00209	-0.03995	0.83497	0.00055	0.00733
B3P86/6-311++G(2d,2p)	0.00212	-0.03940	0.80911	0.00056	0.00739
B3P86/ cc-pVQZ	0.00210	-0.03722	0.73740	0.00056	0.00717
B3PW91/6-311++G(3df,3pd)	0.00209	-0.03969	0.83390	0.00055	0.00733
B3PW91/6-311++G(2d,2p)	0.00211	-0.03918	0.81033	0.00055	0.00740
B3PW91/ cc-pVQZ	0.00209	-0.03683	0.73215	0.00055	0.00716
Ref.[18][a]	0.00207	-0.03719	0.75682	0.00053	0.00714

[a] CCSD(T)/cc-pVQZ.

Table 6: Sextic centrifugal distortion constants of PO_2^-(cm^{-1}).

Method	$\phi_J \times 10^{12}$	$\phi_{JK} \times 10^9$	$\phi_{KJ} \times 10^7$	$\phi_K \times 10^{11}$	$\phi_J \times 10^{12}$	$\phi_{JK} \times 10^{12}$	$\phi_K \times 10^9$
MP2/6-311++G(3df,3pd)	0.4337042602	-0.7600697387	0.1521708805	-0.07796872887	0.2056376716	0.3071883727	0.5817236647
Mp2/6-311++G(2d,2p)	0.4317390142	-0.6872559246	0.1389457913	-0.1789465005	0.2047706211	0.3442661695	0.5600134887
MP2/cc-pVQZ	0.4222161966	-0.6373693851	0.1189104805	-0.07383954558	0.2003503991	0.3044615038	0.4982376678
B3LYP/6-311++G(3df,3pd)	0.4411886037	-0.6657986173	0.1293277377	-0.1319433015	0.2080252642	0.4249060292	0.5276189737
B3LYP/6-311++G(2d,2p)	0.4476606838	-0.6513538786	0.1240404278	-0.1383122371	0.2117777296	0.3824001544	0.5213046804
B3LYP/ cc-pVQZ	0.4289357765	-0.5603425486	0.1008260760	-0.1134571952	0.2029298641	0.3830845170	0.4526350969
B3P86/6-311++G(3df,3pd)	0.4472354979	-0.6563767458	0.1260793417	-0.1297002884	0.2104980248	0.4512981951	0.519780323
B3P86/6-311++G(2d,2p)	0.4552159147	-0.6379351192	0.1199755595	-0.1393767016	0.2147692027	0.4263988156	0.5112706188
B3P86/ cc-pVQZ	0.4367850580	-0.5618851407	0.1008381434	-0.1161167882	0.2061729061	0.4145017620	0.4531178964
B3PW91/6-311++G(3df,3pd)	0.4431376463	-0.6528457894	0.1258723751	-0.1329112161	0.2088008054	0.4319333008	0.5190168616
B3PW91/6-311++G(2d,2p)	0.4509444891	-0.6363297785	0.1203755914	-0.1434693405	0.2129217460	0.4092602033	0.5120983449
B3PW91/ cc-pVQZ	0.4322431831	-0.5540928779	0.09956135951	-0.1195916518	0.2042210826	0.3977342336	0.4495272702

calculated values can be found in Ref. [18]. The anharmonic constants depend on the quadratic, cubic, and quartic force fields. Strong anharmonic interactions between fundamentals and overtones or combination states may lead to a breakdown of the corresponding perturbational formulas. It is then necessary to define the effective constants by excluding the respective contributions from the perturbational summations. One can easily find that our calculated anharmonic constants of PO_2^- anion are in good agreement with the previous calculated results [18]. The corresponding value has the same sign and reasonable magnitude. The calculated anharmonic constants of PO_2^- anion at the B3LYP/cc-pVQZ level can serve as predictions.

The theoretical results of the equilibrium quartic centrifugal distortion constants of PO_2^- are shown in the Table 5. But no experimental results are available for the quartic centrifugal distortion constants. The calculated centrifugal distortion constants, Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K, are numerically close for each theoretical level. The calculated values at the B3P86/cc-pVQZ level are in the excellent agreement with the previous values [18] and can provide the good prediction for the experimental observation of the quartic centrifugal distortion constants of PO_2^-.

Table 7: Coriolis coupling constants of PO_2^-(cm^{-1}).

Method	ζ_{31}	ζ_{32}
MP2/6-311++G(3df,3pd)	0.32287	0.94644
Mp2/6-311++G(2d,2p)	0.32852	0.94450
MP2/cc-pVQZ	0.33337	0.94280
B3LYP/6-311++G(3df,3pd)	0.32094	0.94710
B3LYP/6-311++G(2d,2p)	0.32657	0.94517
B3LYP/ cc-pVQZ	0.33116	0.94358
B3P86/6-311++G(3df,3pd)	0.32159	0.94688
B3P86/6-311++G(2d,2p)	0.32703	0.94502
B3P86/ cc-pVQZ	0.33067	0.94375
B3PW91/6-311++G(3df,3pd)	0.32147	0.94692
B3PW91/6-311++G(2d,2p)	0.32719	0.94496
B3PW91/ cc-pVQZ	0.33117	0.94357
Ref.[18][a]	0.3314	-0.9435

[a] CCSD(T)/cc-pVQZ.

Table 8: Cubic force constants of PO_2^-(cm^{-1}).

Method	F_{111}	F_{211}	F_{221}	F_{222}	F_{331}	F_{333}
MP2/6-311++G(3df,3pd)	-216.08255	40.23290	32.97180	33.26217	-277.60340	-8.42839
Mp2/6-311++G(2d,2p)	-213.99203	40.60824	29.16938	28.36149	-275.05648	-5.14581
MP2/cc-pVQZ	-216.04619	40.70544	29.82897	33.58312	-273.64276	-4.61841
B3LYP/6-311++G(3df,3pd)	-214.23578	39.08194	34.18457	31.43897	-278.68586	-12.13134
B3LYP/6-311++G(2d,2p)	-212.98423	40.53247	32.18499	31.22425	-278.02404	-8.22893
B3LYP/ cc-pVQZ	-214.33576	39.65194	30.11327	32.48885	-275.74615	-7.90451
B3P86/6-311++G(3df,3pd)	-213.77154	39.34357	35.26270	31.27416	-278.00698	-12.44259
B3P86/6-311++G(2d,2p)	-212.41178	40.49930	33.36730	30.80469	-276.93506	-9.04644
B3P86/ cc-pVQZ	-213.77328	39.87282	31.64805	32.09653	-275.38853	-8.59941
B3PW91/6-311++G(3df,3pd)	-213.33711	39.51540	34.55761	31.07641	-277.82334	-11.68968
B3PW91/6-311++G(2d,2p)	-211.64530	40.72966	32.71619	30.56926	-276.40272	-8.18379
B3PW91/ cc-pVQZ	-213.00169	40.06240	30.75670	31.86781	-274.81580	-7.66016

The calculated sextic centrifugal distortion constants of PO_2^- anion are listed in the Table 6. It is clearly that they have the same sign and the right order of the magnitude. Further, there is a very small difference among these seven values from the various different calculations. Unfortunately, the experimental and theoretical sextic centrifugal distortion constants of PO_2^- have not been reported so far. Therefore, our calculated results can be treated as the predictions of sextic centrifugal distortion constants of PO_2^-.

The computed coriolis coupling constants of PO_2^- anion are presented in the Table 7. The coriolis coupling constants for PO_2^- have no corresponding experimental data and only a previous calculation at CCSD(T)/cc-pVQZ level [18]. As far as we know, coriolis coupling constant connects the ω_i mode and the ω_j mode. It is then obvious that ζ_{31} stands the coupling of the asymmetric stretching mode and the symmetric stretching mode ω_1; ζ_{32} is the constant connecting ω_3 and the bending mode ω_2. Surprisingly, our calculated ζ_{32} from our methods is positive, however, the ζ_{32} from Ref. [18] is negative.

Table 9: Quartic force constants of PO_2^-(cm^{-1}).

Method	F_{1111}	F_{2111}	F_{2211}	F_{2221}	F_{2222}	F_{3311}	F_{3321}	F_{3322}	F_{3333}
MP2/6-311++G(3df,3pd)	37.02635	-15.38466	-15.52887	-1.71744	1.29339	55.09293	-0.44698	-23.66564	61.31377
Mp2/6-311++G(2d,2p)	37.41869	-15.88881	-14.81192	-1.34121	-0.79390	55.83472	-0.97856	-22.68676	61.60283
MP2/cc-pVQZ	36.56692	-15.54583	-14.54481	-1.52377	3.43259	54.07076	-1.37006	-22.65593	59.98386
B3LYP/6-311++G(3df,3pd)	33.63873	-13.17717	-15.83586	-1.31161	3.73975	49.54865	2.68258	-24.58530	53.43160
B3LYP/6-311++G(2d,2p)	33.77450	-13.40706	-15.32510	-1.09800	3.97847	49.85508	2.48916	-24.10537	53.63606
B3LYP/ cc-pVQZ	34.26648	-13.56572	-14.69963	-1.07988	5.51947	50.17126	1.33703	-23.43350	54.50712
B3P86/6-311++G(3df,3pd)	34.33995	-13.79840	-15.60200	-1.38528	4.10513	50.81078	1.62780	-24.20811	55.61291
B3P86/6-311++G(2d,2p)	33.80949	-13.93331	-15.14912	-1.21147	4.27861	50.25759	1.58634	-23.78188	54.66253
B3P86/ cc-pVQZ	34.66939	-14.15532	-14.49265	-1.08978	5.82779	51.17639	0.37191	-23.03080	56.50445
B3PW91/6-311++G(3df,3pd)	34.98423	-13.82858	-15.40148	-1.34665	3.70630	51.64979	1.41174	-24.02516	56.84474
B3PW91/6-311++G(2d,2p)	34.42571	-14.16561	-14.74105	-1.16042	4.11380	51.28425	0.96261	-23.31922	56.53602
B3PW91/ cc-pVQZ	35.22209	-14.24205	-14.15866	-1.06653	5.50263	51.96893	-	-22.72267	57.84120

The difference in sign may be due to the typing error.

Tables 8-9 provide the calculated cubic and quartic force constants of the PO_2^- anion. By definition, the quadratic normal coordinate constants correspond to the harmonic frequencies ω_i(i=1, 2, 3). They have been discussed in Table 1. we think that the B3P86/cc-pVQZ level gives the good results for the cubic and quartic force constants of PO_2^-. In fact, the results calculated by the DFT method are close to each other including the same sign and order of magnitude.

4 Conclusions

The spectroscopic constants and anharmonic force field of PO_2^- are investigated employing MP2, B3LYP, B3P86, B3PW91 methods with 6-311++G(3df,3pd), 6-311++G(2d,2p)Aand cc-pVQZ basis sets. The DFT results, especially the B3P86 method, are in the good agreement with the previous available experimental or theoretical data. The predictions for experimentally unknown spectroscopic constants are expected to guide the future high-resolution experimental work of PO_2^-. Our calculations are also shown that the adding polarized functions produce a substantial improvement in the predicted structure.

All the spectroscopic constants depend on the cubic and quartic force field of PO_2^-. Therefore, the formula of these spectroscopic constants in terms of the potential energy derivatives will be followed.

$$
\begin{aligned}
E(v,J)=G(v)+F_v(J)=&\sum_i \omega_i\left(v_i+\frac{1}{2}\right)+\sum_{i\le j} X_{ij}\left(v_i+\frac{1}{2}\right)\left(v_j+\frac{1}{2}\right)+AJ_z^2+BJ_x^2+CJ_y^2\\
&-\Delta_J J^4-\Delta_{JK}J^2J_z^2-\Delta_K J_z^4-2\delta_J J^2(J_x^2-J_y^2)-\delta_K[J_z^2(J_x^2-J_y^2)\\
&+(J_x^2-J_y^2)J_z^2]+\phi_J J^6+\phi_{JK}J^4J_z^2+\phi_{KJ}J^2J_z^4+\phi_K J_z^6+2\varphi_J J^4(J_x^2-J_y^2)\\
&+\varphi_{JK}J^2[J_z^2(J_x^2-J_y^2)+(J_x^2-J_y^2)J_z^2]+\varphi_K[J_z^4(J_x^2-J_y^2)+(J_x^2-J_y^2)J_z^2]
\end{aligned}
$$

In the above equation, $G(v)$ is the vibrational term and $F_v(J)$ is the rotational term. Submitting the parameters in Tables 1, 2, 5, 6, and 7 into the above equation, one can obtain the calculated rotational energy of PO_2^-.

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