

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

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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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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 vibrational frequencies $\omega_1=1097\text{cm}^{-1}$, $\omega_2=501\text{cm}^{-1}$ and $\omega_3=1207\text{cm}^{-1}$, which was used to calculate the P-O bond length $r_{PO}=1.65\text{Å}$ and the OPO angle $\theta_{OPO}=110^\circ$. 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: $r_{PO}=1.50\pm 0.01\text{Å}$, $\theta_{OPO}=120.0\pm 0.1^\circ$ 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, $r_{PO}=1.504\pm 0.005\text{Å}$ and $\theta_{OPO}=119.0\pm 0.2^\circ$ 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, $r_{PO}=1.495\pm 0.005\text{Å}$ and $\theta_{OPO}=119.5\pm 0.5^\circ$ 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