高等学校化学学报 2007 28 (11): 2183-2186 ISSN: 0251-0790 CN: 22-1131/O6

研究论文

OClO里德堡态激发能的准确预测及其阴离子低能激发态的从头算研究

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收稿日期 2006-3-31 修回日期 网络版发布日期 2007-11-12 接受日期

摘要 采用全活化空间自洽场方法(CASSCF)研究了OClO阴离子7个低能电子态及其自由基的基态. 为了进一步考虑动态电子相关效应, 采用二级多组态微扰理论(CASPT2)获得更加可靠的能量值. 此外, 在ANO-L基组的基础上, 在OClO自由基的电荷中心增加了为研究里德堡态所建立的1*s*1*p*1*d*的波函数, 并应用多组态二级微扰理论(MS-CASPT2)方法获得了里德堡态的准确电子激发能.

关键词 OClO 全活化空间自洽场方法 二级多组态微扰理论 激发态 里德堡态

分类号 O641

DOI:

Accurate Prediction of Excited Energy of Rydberg States of OClO and Ab Initio Investigation of Excited States of OClO Anion with a Low Energy

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Received 2006-3-31 Revised Online 2007-11-12 Accepted

Abstract By using the complete active space self-consistent field (CASSCF) method with large atomic natural orbital (ANO-L) basis set, seven electronic states of the OClO- anion were calculated. The optimized geometry of the ground state with ANO basis set agrees better with the experimental and previous theoretical values. Furthermore, the stable geometries of three singlet and three triplet excited states were obtained. Taking the further correlation effects into account, the second-order perturbation (CASPT2) calculations were carried out for the energetic calibration. Furthermore, the Rydberg states of the OClO radical were investigated by using multiconfigurational CASPT2 (MS-CASPT2) theory under the basis set of ANO-L functions augmented with an adapted 1*s*1*p*1*d* Rydberg functions that have specially been built for this study. Ten electronic excited states were found for the transition from $3b_1$ electron into the Rydberg orbitals. The $3b_1 \rightarrow ns$ and $3b_1 \rightarrow np$ series agreed excellent with the experimental values, and the assignment of $3b_1 \rightarrow 3d$ series supported the results of Marston. Meanwhile, two and four Rydberg states were computed for the transition of $1a_2$ and $5b_2$ electron, respectively.

Key words OCIO; Complete active space self-consistent field(CASSCF); Second-oder perturbation(CASPT2); Excited state; Rydberg state

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