

Ab Initio 방법에 의한 KCs 분자 전자상태들의 특성조사

Study on the Characteristics of the Electronic States of KCs Molecule with Ab Initio Method

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Recent progress in cold molecule formation of heteronuclear molecule such as KRb, RbCs, etc. provides routes for population transfer to the ground state, which give basic information for q-bit processing by using polar molecule in the external electric field although the experiments with rotational resolution need to be done.

There are few theoretical and experimental investigations for polar molecule such as KCs compared with other polar molecule such as KRb, RbCs, NaRb, etc. Also there is no photoassociation study for this molecule so that it is challenging to do experiment for this molecule. We should obtain the theoretical and experimental data for those electronic states of heteronuclear diatomic molecule because it is not well known for the excited states of these molecules due to complex electronic structure and the perturbation between the states to transfer the population to the ground state. Recently the channel coupling deperturbation methods provided pathways to solve the perturbation problems in RbCs and NaRb. However, we need the informations such as the R-dependent spin-orbit function to do this deperturbation analysis. There is no information of R-dependent spin-orbit function for KCs although there is spin-orbit splitting at the near dissociation limit. Except this permanent dipole moment, potential energy curves, transition dipole moments, etc. should be investigated.

Ab initio calculations for heteronuclear molecule such as KCs, KRb, and RbCs, etc. have been done by several theoreticians. Korek et al.^[1,2] calculated ab initio calculation for KCs based on nonempirical pseudopotentials so that the 72 lowest molecular states were obtained. For KCs there is one theoretical evaluation for the permanent dipole moment^[2] by using different method from our method. These calculations give quite different values according to the theoretical basis. The reasons for these differences are not known well yet.

We used effective small core (9 valence electrons) quasi-relativistic pseudopotentials. Valence-valence and core-valence electronic correlation have been taken accounted by full valance configuration interaction method combined with one-electron core polarization potentials. The energy and relevant electronic matrix elements were evaluated in the basis of the spin-averaged wavefunctions corresponding to pure Hund's case (a) coupling scheme and compared with others^[1,2].

The adiabatic potential energy curves (PECs), permanent dipole moments as well as spin-orbit

and angular coupling matrix elements have been obtained in a wide range internuclear distances using large-scale multi-reference configuration interaction (MR-CI) calculation on effective small core (9-electrons) pseudopotentials (ECP). One-electron l -independent core-polarization potentials (CPP) were employed together with the above small core ECPs to take into account partly core-polarization effects. The corresponding ECP spin-orbit basis coefficients and CPP cutoff radii were adjusted for each atom in order to reproduce experimental fine-structure energy of both $4^2p(K)$ and $6^2p(Cs)$ excited states. The PECs and relevant electronic matrix elements were evaluated in the basis of the zeroth-order (spin-averaged) MRCI wavefunctions corresponding to pure Hund's case (a) coupling scheme. Additionally, the Hund's case (c) PECs were evaluated by the state-interacting method which means that the spin-orbit eigenstates were obtained by diagonalizing $H_{el.} + H_{SO}$ Hamiltonian in a basis of Hund's case (a) eigenfunctions of $H_{el.}$ All calculations were performed by means of the MOLPRO program package^[3]. The inner core shells of the potassium and cesium atoms were replaced by spin-orbit averaged non-empirical effective core pseudopotentials (ECP), leaving 9 valence electrons (9-ve) of each atom for explicit treatment. Both shape and energy consistent ECPs were used for a comparison reason. The relevant unconstructed spin-averaged and spin-orbit Gaussian basis sets used for each atom were borrowed from the above references^[4]. Shape-consistent ECPs were augmented by diffuse parts of the "all-electron" bases for electric property calculation and extended by additional diffuse and polarization functions. The optimized molecular orbitals were constructed from the solutions of the state-average complete active space self-consistent field (SA-CASSCF) problem for the lowest $(1-4)^{1,3}\Sigma^+$ and $(1-3)^{1,3}\Pi$ electronic states taken with equal weights. The dynamical correlation effects were introduced by internally contracted multi-reference configuration interaction method which was applied for only two valence electrons keeping the rest frozen, i.e., in a full valence (2-electrons) CI scheme. Active space consisted of 14s and 10p orbitals. Potential energy curves (PECs), the R-dependent spin-orbit interaction and permanent dipole moments (EPDMs) have been estimated for all states converging to the lowest three $4s(K)+6s(Cs)$, $4s(K)+6p(Cs)$, $4p(K)+5s(Cs)$ dissociation limits.

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