

LONG-RANGE RELATIVISTIC INTERACTIONS AND PHOTOASSOCIATION DYNAMICS OF COLD CALCIUM ATOMS

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State-of-the-art ab initio techniques have been applied to compute all potential energy curves for the excited states of the calcium dimer in the Born-Oppenheimer approximation corresponding to the lowest atomic dissociations, $^3P + ^1S$, $^3D + ^1S$, $^1D + ^1S$, and $^1P + ^1S$. The potentials were corrected for the relativistic terms resulting from the many-electron Breit theory to the first-order in α^2 . The spin-orbit coupling matrix elements with the full spin-orbit Hamiltonian and the nonadiabatic coupling terms were obtained from multireference configuration interaction calculations restricted to single and double excitations. The long range theory of the spin-orbit coupling matrix elements has been worked out, and explicit expressions for the leading coefficients governing the asymptotics were derived, but cannot be computed with the standard programs of quantum chemistry. It is shown that if the spin-orbit coupling is properly accounted for the potentials for the 0_u^+ and 1_u states show the same $1/R$ dependence in the long range as the potentials for the singlet states, i.e. the long range of the corresponding curves is governed by relativistic resonant interactions with an R^{-3} and R^{-5} asymptotics for the $^3P + ^1S$ and $^3D + ^1S$ dissociations, respectively. The results of ab initio calculations were used in nearly exact nonadiabatic calculations of the ro-vibrational energy levels and photoassociation intensities at ultralow temperatures. Unfortunately, the R^{-3} dependence of the relativistic potentials does not show up in the computed spectra due to inaccuracies in the computed spin-orbit coupling matrix elements at large interatomic distances.