Ab initio calculation of radiative properties of the RbAr exciplex

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The precise non-empirical estimation of the lifetimes of the rovibrational levels, belonging to the low-lying excited electronic states of the RbAr exciplex, is carried out. The obtained data are required for the further optimization of the optical pumping conditions of the promising alkali metal – inert gas laser media [1].

Inner electronic shells of both atoms are replaced by the 2-component shape-consistent effective core pseudopotentials [2,3], leaving 9 and 8 electrons of Rb and Ar respectively for the explicit treatment. The spatial parts of the one-electron pseudospinors are expanded in the set of the Gaussian-type functions. For Rb the optimized 7s7p5d3f1g basis set is used. For Ar the augmented quadruple-zeta set is applied. Energy of the ground and excited Ω=(1-3)1/2, (1)3/2 electronic RbAr states is calculated by the multireference relativistic Fock space coupled cluster method with singles and doubles (RFSCC, [4]). Excited state potential energy functions were obtained by combining the calculated energy differences with accurate CCSD(T) potential energy curve (PEC) for the ground state. The transition dipole moments (TDMs) are calculated by the finite-field method, formulated for the effective Hamiltonian [5]. Rovibrational energies and wavefunctions are found by the finite-difference method [6].

The obtained lifetimes of the free Rb (5p) ^2P_J (J=1/2, 3/2) states deviate from the experimental ones by 0.3%. In case of the RbAr exciplex the accuracy should not decrease dramatically, as the reliability of the PECs and TDMs in the wide range of internuclear distances is ensured by the size-consistency of the RFSCC method along with the stability of the calculated values under further extension of the basis sets.

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