Quasi-relativistic treatment of the low-lying KRb states

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Nowadays the rigorous coupled-channel (CC) deperturbation analysis is the well-established procedure for accurate representation of strongly interacting electronic states. The practical implementation of the CC approach is based on the explicit knowledge of the potential energy curves, non-adiabatic electronic matrix elements and transition dipole moments as function of internuclear distance. The high level *ab initio* electronic structure calculation is apparently the most straightforward way of generating all required matrix elements. The close energies of the K and Rb atoms in their first excited ^{2}P states indispensably lead to the high density of the strongly coupled molecular states. Moreover, for KRb molecule the spin-orbit (SO) coupling effect becomes comparable with the vibrational spacing even for small and intermediate interatomic distances where smooth transformation between pure (**a**) to (**c**) Hund's coupling cases take places.

We present the spin-orbit, angular and radial coupling matrix elements among all strongly coupled electronic states converging to the lowest three dissociation limits of KRb molecules. The non-adiabatic matrix elements have been obtained in a wide range internuclear distances by using of both shape and energy consistent small (9-electrons) effective core pseudopotentials (ECP). The dynamic correlation has been accounted for a large scale 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. The angular independent core-polarization potentials (CPP) were employed together with the above small core ECPs to take into account for implicitly the residual core-valence effect. The relevant adiabatic potential energy curves and electric dipole transition moments were evaluated as well. All electronic structure calculations were performed in the framework of a quasi-relativistic (**a**) Hund's case coupling scheme by means of the MOLPRO program package [1]. The possible application of the *ab initio* functions for modelling of the energy and radiative properties of the spin-orbit A~b complex of KRb is discussed [2,3]. The reliability of the results is fragmentally probed by a comparison with preceding calculations.

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[1] MOLPRO, Version 2010.1, a package of *ab initio* programs, H.-J. Werner, P. J. Knowles et al.
[2] J.-T. Kim et al., *New J. Phys.* **2009**, *11*, 055020.
[3] E. A. Pazyuk et al., *ECAMP11* **2013**.