

Theoretical study of non-adiabatic coupling among KRb low-lying states

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The rigorous deperturbation analysis is indispensably required for accurate representation of fully mixed electronic states, especially in vicinity of their dissociation limits where the density of the mutually interacted rovibronic levels increases significantly. For heavy alkali atom (like Rb and Cs) containing molecules the spin-orbit (SO) coupling effect becomes dominating, among other non-adiabatic interactions, even for small and intermediate interatomic distances where smooth transformation between pure (**a**) to (**c**) Hund's coupling cases take places. Although the both coupling cases are mathematically equivalents the (**a**)-case looks more preferable for the practical deperturbation treatment since the relevant SO matrix elements are usually smooth function of r comparing with the corresponding radial coupling matrix elements which are singular in vicinity of the avoided crossing points of the adiabatic relativistic potentials obtained in (**c**) Hund's coupling case.

The coupled-channel (CC) deperturbation analysis recently became the well-established procedure for solving the above rovibronic problem with acceptable (experimental) accuracy. However, the practical implementation of the CC approach is based on the explicit knowledge (and relevant parameterization) of the non-adiabatic electronic matrix elements as function of r . The high level *ab initio* electronic structure calculation is apparently the most straightforward way of generating the required matrix elements.

We report here the spin-orbit, angular and radial coupling matrix elements required for global deperturbation treatment of 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 a pure (**a**) Hund's case coupling scheme by means of the MOLPRO program package [1].

The application of the *ab initio* functions for modelling of the energy and radiative properties of KRb beyond the adiabatic approximation is discussed [2,3]. The reliability of the results is fragmentally probed by a comparison with preceding calculations and experiments.

References:

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