

Towards the Experimental Accuracy of Relativistic Coupled Cluster Calculations on Excited States of Alkali Diatomics

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The achieved accuracy in the relative positions of the *ab initio* relativistic adiabatic and quasi-diabatic potential energy curves for the excited states provides unambiguous vibrational assignment of the strongly spin-orbit coupled diatomic states. A few percent of systematic error in the calculated transition dipole moments is comparable and even less than the typical uncertainty of the measured relative intensity distribution.

Relativistic electronic structure model

Accurate shape-consistent two-component pseudopotentials leaving nine electrons of each atom for explicit correlation treatment. The pseudopotentials were derived from the valence-shell solutions of the atomic Dirac–Fock–Breit equations with the Fermi nuclear charge model.

Relativistic Multireference Fock-Space Coupled Cluster method (FS-RCC): conventional FSRCC equations are nearly useless because of numerical instabilities (“intruder state problem”)

$$t_K = \frac{1}{D_K} \left(\overline{V\Omega} - \overline{\Omega} \overline{(V\Omega)}_{Cl} \right)_K \quad (1)$$

Instabilities are avoided through introducing adjustable shifts of energy denominators D_k in a way ensuring minimum damage of low-lying target states [1]

$$D'_K = D_K + S_K \left(\frac{S_K}{D_K + S_K} \right)^n, \quad n \geq 1.$$

n is the shift attenuation parameter. The larger the n value, the less efficient the shifting of “good” (large negative) energy denominators



sequence of effective Hamiltonians obtained by solving the modified FSRCC equations with increasing n

$$n = 1, 2, \dots \implies \tilde{H}_1, \tilde{H}_2,$$

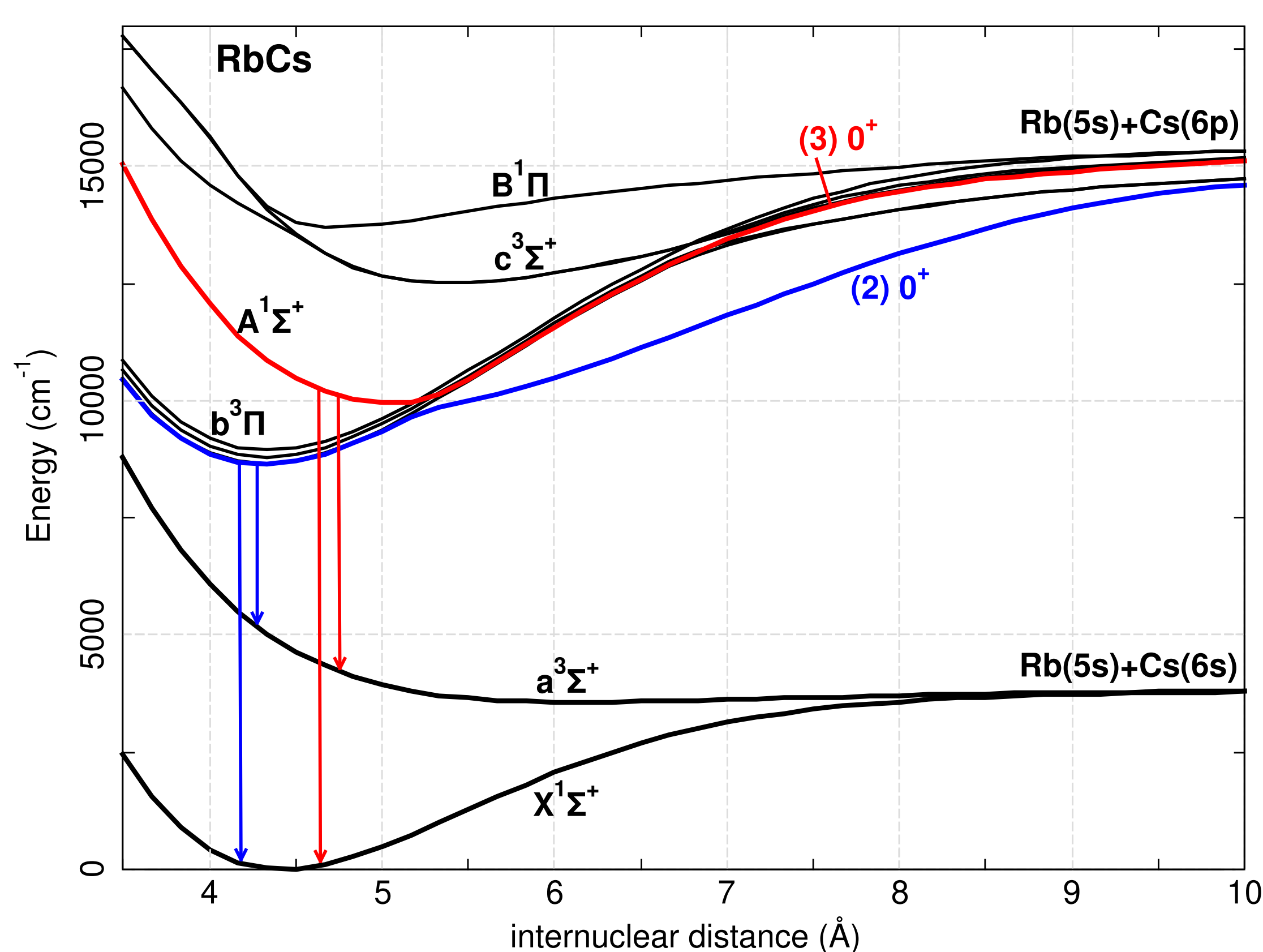
extrapolation of the sequence of low-energy fragments of \tilde{H}_n to $n = \infty$ (\approx shifts switched off) [2]



adiabatic energies and model space projections of the wavefunctions for low-lying electronic states

Software. Calculations were performed with the modified DIRAC software [3] and our completely new FS-RCC code **EXP-T**.

Potential energy curves



The potential energy curves for the adiabatic excited states were constructed by adding the FSRCC excitation energies as functions of the internuclear separation to the highly accurate empirical ground-state potential

$$E_i^{ad}(R) = E_{X,emp}^{ad}(R) + \left(E_{i,FSRCC}^{ad}(R) - E_{X,FSRCC}^{ad}(R) \right)$$

Quasidiabatization by projecting

To convert the adiabatic spin-orbit-coupled states into quasidiabatic states we applied the quasidiabatization by projecting technique [1]

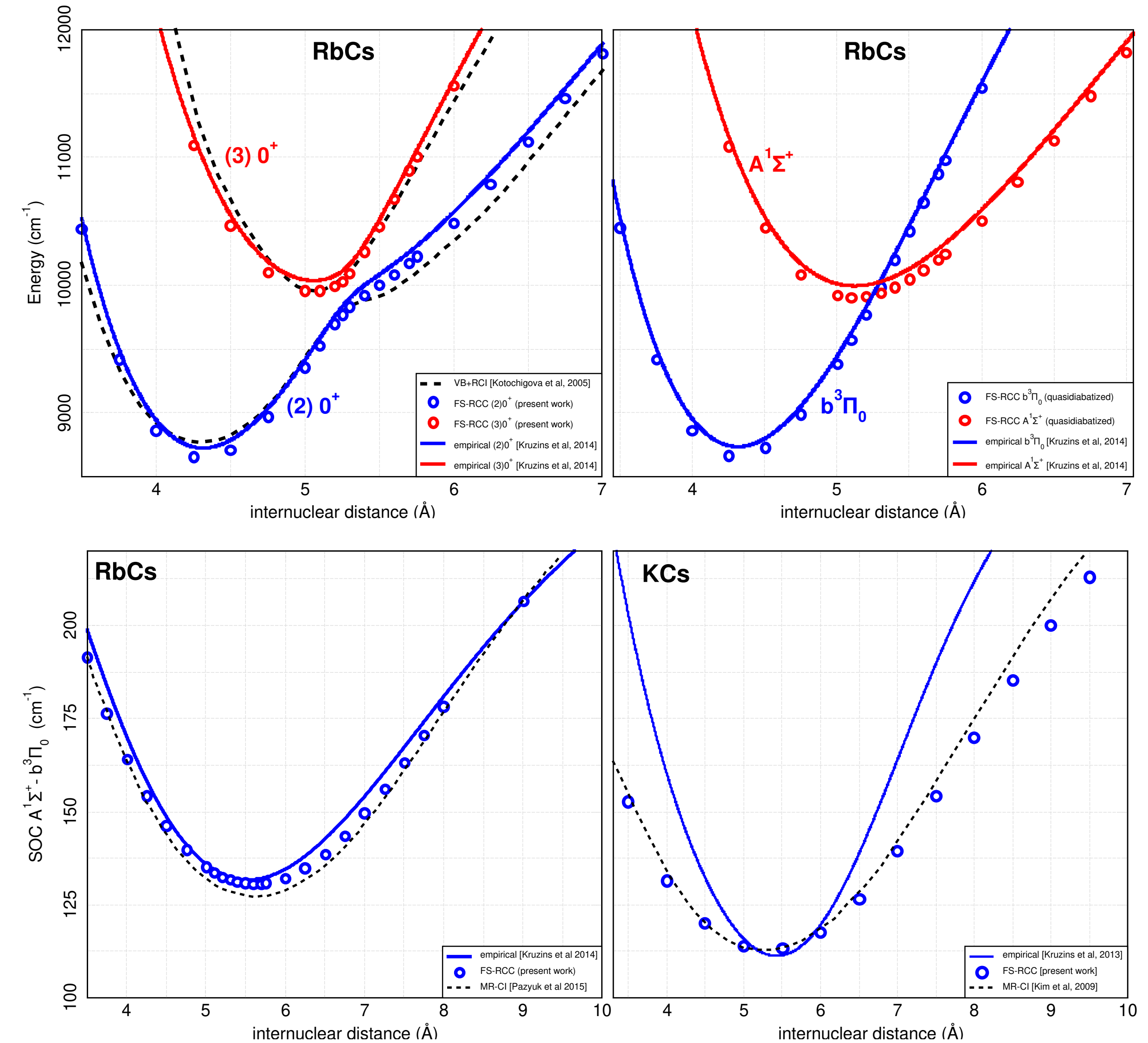
Quasidiabatic energies: $\langle \phi_i | H | \phi_i \rangle$

“Spin-orbit couplings”: $\langle \phi_i | H | \phi_j \rangle, i \neq j$

H total relativistic Hamiltonian

ϕ_i orthogonalized projections of eigenstates of the scalar relativistic counterpart of H onto the subspace of strongly coupled H eigenstates $\{\psi_i\}$

- fully consistent with the results of the local deperturbation analysis of experimental data:



Despite the small systematic error the FS-RCC method makes it possible to achieve unambiguous vibrational assignment!

Transition electric dipole moment calculations

Electric transition dipole moments $\langle \psi_i | M_\eta | \psi_f \rangle$ were estimated using the finite-field technique:

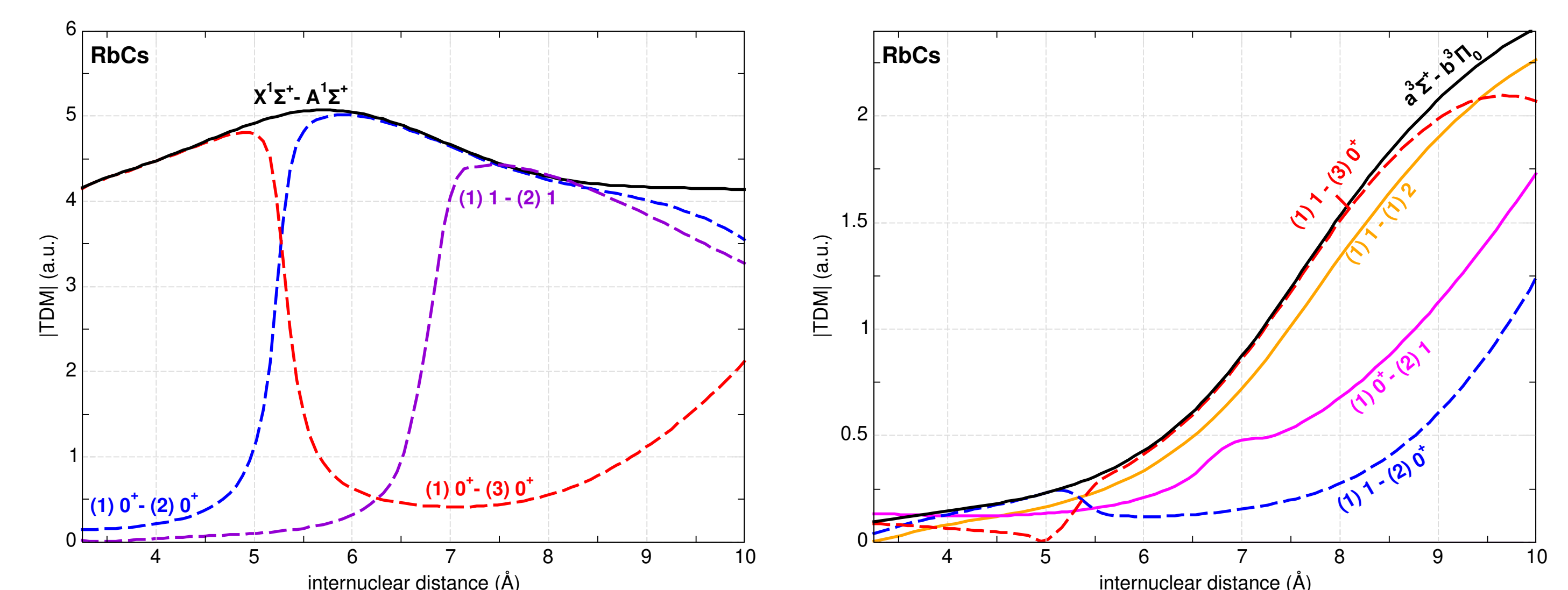
$$\langle \psi_i | M_\eta | \psi_f \rangle \approx (E_f - E_i) \frac{\langle \tilde{\psi}_i^{\perp\perp}(\Delta F_\eta) | \tilde{\psi}_f(-\Delta F_\eta) \rangle}{2\Delta F_\eta}, \quad \eta = x, y, z$$

F applied uniform electric field strength ($\sim 10^{-5}$ a.u.)

$\tilde{\psi}_i^{\perp\perp}, \tilde{\psi}_f$ left and right effective Hamiltonian eigenvectors

$E_f - E_i$ transition energy

- only the model space projections of many-electron wavefunctions are used
- main contributions from the remainder parts of wavefunctions are implicitly incorporated
- correct up to the terms linear in cluster amplitudes inclusively
- transition moment components for all pairs of initial and final states are obtained simultaneously



Bibliography

- [1] A. Zaitsevskii et al. Phys. Rev. A. 96, 022516 (2017)
- [2] A. Zaitsevskii, E. Eliav. Int. J. Quantum Chem. 118, e25772 (2018)
- [3] L. Visscher et al., DIRAC, a relativistic ab initio electronic structure program, <http://www.diracprogram.org>