

EXPERIMENTAL AND COMPUTATIONAL STUDY OF THE SPIN-ORBIT COUPLING EFFECT IN $(2)^1\Pi$ KCs

A.Stolyarov², E.Pazyuk², M.Tamanis¹, L.Busevica¹,
R.Ferber¹, I. Klincare¹, O. Nikolayeva¹

¹Laser Centre, University of Latvia, 19 Rainis Boulevard, Riga, LV-1586, LATVIA

²Department of Chemistry, Moscow State University, Leninskije Gori 1/3, Moscow,
RUSSIA

The pronounced spin-orbit coupling (SOC) effect takes place among the most low-lying excited states of heavy alkali dimers opening a window for two-step optical conversion of the colliding pairs of the respective ultracold atoms into their stable ground molecular state. The SOC effect is typically observed in spectra as an abrupt or/and systematic shift of energy levels from their adiabatic positions. These energy non-adiabatic shifts are often accompanied by appearance of the spin-forbidden singlet-triplet transitions originating from the strongly perturbed levels.

Here we present both experimental and computational study of the excited $(2)D^1\Pi$ state of KCs which are perturbed by the nearby triplet $(2)d^3\Pi$ state $(3)e^3\Sigma^+$ states converging to the same $(4P)K+(6S)Cs$ limit. Energy measurements were performed by high resolution Fourier-transform spectroscopy of the $(2)D^1\Pi \rightarrow X^1\Sigma^+$ laser induced fluorescence (LIF) spectra. Rotational assignment of the transitions was facilitated by very accurate ground $X^1\Sigma^+$ state PEC [1] while the absolute vibrational numbering of the $D^1\Pi$ state was established by using of experimental intensity distributions in the $D \rightarrow X$ LIF series originating from the low-lying D-state levels. As the result, about 1200 rovibronic term values assigned to the regularly and locally perturbed levels of the most abundant $^{39}K^{133}Cs$ isotopomer were obtained with ca. 0.01 cm^{-1} uncertainty in energy range from ca. 15500 cm^{-1} to 17260 cm^{-1} and J' range from 7 to 265.

We were not able to reproduce the experimental term values by a single adiabatic PEC of the $(2)D^1\Pi$ state. This suggests that the state is markedly perturbed in spite of the fact that only from few levels we observed fluorescence to the ground triplet $a^3\Sigma^+$ state. Therefore, rigorous channel-coupled deperturbation model had to be introduced to account for SOC between the $D^1\Pi$, $d^3\Pi$ and $e^3\Sigma^+$ states. The required SO matrix elements were evaluated in the basis of the spin-averaged wavefunctions corresponding to pure Hund's coupling case (**a**) by using of small effective core pseudopotentials of both atoms. The deperturbed diabatic PECs for the interacting states were defined analytically by Extended Morse Oscillator model. Adaptive mapping procedure was used to improve the efficiency of solution of the set of coupled radial equations. The completeness of the deperturbation analysis is confirmed by a good agreement of the term values predicted for the $^{41}K^{133}Cs$ isotopomer and rovibronic probabilities for the spin-forbidden $(2)D^1\Pi \rightarrow a^3\Sigma^+$ transition with their relevant experimental counterparts.

[1] R. Ferber, I. Klincare, O. Nikolayeva, M. Tamanis, H. Knöckel, E. Tiemann, and A. Pashov, *J. Chem. Phys.* **128**, 244316 (2008).