ESR SPECTRA OF ALKALI-METAL ATOMS ON HELIUM NANODROPLETS: A THEORETICAL MODEL FOR THE PREDICTION OF HELIUM INDUCED HYPERFINE STRUCTURE SHIFTS

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We predict He-droplet-induced changes of the isotropic HFS constant a_{HFS} of the alkali-metal atoms M = Li, Na, K and Rb on the basis of a model description. Optically detected electron spin resonance spectroscopy[a] has allowed high resolution measurements that show the influence of the helium droplet and its size on the unpaired electron spin density at the alkali nucleus[b]. Our theoretical approach[c] to describe this dependence is based on a combination of two well established techniques: Results of relativistic coupled-cluster calculations on the alkali-He dimers (energy and HFS constant as functions of the binding length) are mapped onto the doped-droplet-situation with the help of helium-density functional theory. We simulate doped droplets He_N with N ranging from 50 to 10000, using the diatomic alkali-He-potential energy curves as input. From the obtained density profiles we evaluate average distances between the dopant atom and its direct helium neighborhood. The distances are then set in relation to the variation of the HFS constant with binding length in the simplified alkali-He-dimer model picture. This method yields reliable relative shifts but involves a systematic absolute error. Hence, the absolute values of the shifts are tied to one experimentally determined HFS constant for ^{85}Rb-He$_{N=2000}$. With this parameter choice we obtain results in good agreement with the available experimental data for Rb and K[a,b] confirming the predicted 1/N trend of the functional dependence[c].

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