E ⊗ e VIBRONIC COUPLING IN QUARTET STATES OF Rb_3 AND K_3 ON HELIUM DROPLETS

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We present laser-induced-fluorescence (LIF) and magnetic-circular-dichroism (MCD) spectra of the $(2)\,^4E' \leftarrow (1)\,^4A_2'$ band of Rb_3 and K_3 on He nanodroplets. For Rb_3 we find a progression of four bands, split by spin-orbit (SO) and weakly perturbed by linear vibronic Jahn-Teller (JT) coupling. For K_3 the transition had been previously observed, and interpreted in terms of a linear and quadratic Jahn-Teller coupling in the $(2)\,^4E'$ state.[a] An unambiguous assignment of spectra on He droplets is however difficult due to matrix broadening; MCD spectra are a valuable method to offset this unwanted effect. For K_3 they clearly reveal the importance of SO coupling and suggest a different assignment with weak linear, and no significant quadratic, JT coupling. Further, interpretation of our data in terms of free-molecule SO indicate that the trimers lie flat on the droplet surface. The observed strong $\mathcal{C}$-type MCD spectra arise from different populations of the ground-state Zeeman sublevels; a quantitative analysis allows a determination of the spin temperature, hence of the temperature at the droplet surface. Our simulations are consistent with a value of 0.4 K, which agrees with our previous findings from spectra of triplet-state alkali-metal dimers.[b] This is the first observation of SO coupling in quartet states of trimers.

[a] J. H. Reho, J. Higgins, M. Nooijen, K. K. Lehmann, and G. Scoles, *J. Chem. Phys.* **115,** 10265 (2001).
[b] G. Auböck, J. Nagl, C. Callegari, and W. E. Ernst, *J. Phys. Chem. A* **111,** 7404 (2007).