Unraveling the electronic states of the copper dimer using nonlinear optical spectroscopy

M. Beck[1], B. Visser[1], P. Bornhauser[1], G. Knopp[1], J. A. van Bokhoven[1,2], P. P. Radi[1]*

[1]Paul Scherrer Institut, [2]ETH Zurich

High-resolution optical spectra of transition metal containing molecules and clusters are characterized by dense-lying rotational lines, originating from many overlapping vibrational and electronic bands. The copper dimer is considered to be one of the simplest transition metal systems. However, despite its hydrogen-like ground state, the electronic excited states give rise to complex spectra that are difficult to assign. As a consequence, even for the better characterized high-lying states, fundamental spectroscopic properties like molecular constants and electronic term symbols are missing.

We use Two-Color Resonant Four-Wave Mixing (TC-RFWM) methods to assign the lines of such complex absorption bands. TC-RFWM produces a spatially separated, background-free signal beam from the non-linear interaction of three input beams that overlap within the common focal point in the probe region. In the optically thin environment of a molecular beam, observable TC-RFWM signal generation requires resonance-enhancement by two transitions that share a common level. Therefore, selection rules for optical-optical double resonances apply and reduce the complex spectra to just a few rotational lines which are often assigned in a straightforward manner.

The laser ablation-based cluster source used to prepare the copper dimers in gas phase and the optical setup is described in [1]. Figure 1 shows a selected set of spectra containing rotationally resolved transitions obtained by TC-RFWM. For one isotopologue, extra lines where found and assigned to a perturbing state that is crossing the potential curve of the J-state. Some of these extra lines have already been seen before, but could not be assigned at that time. In the ongoing work, by measuring and assigning unambiguously over 600 lines in the energy range of the I-X and the J-X transitions, a rich network of perturbing states could be identified for several vibronic levels and their molecular constants could be determined. The investigations reveal a detailed picture of the complex bonding structure of this transition metal dimer. This can be used as a benchmark for prospective quantum chemical *ab initio* methods, but is also basis for future studies of heteronuclear transition metal systems.

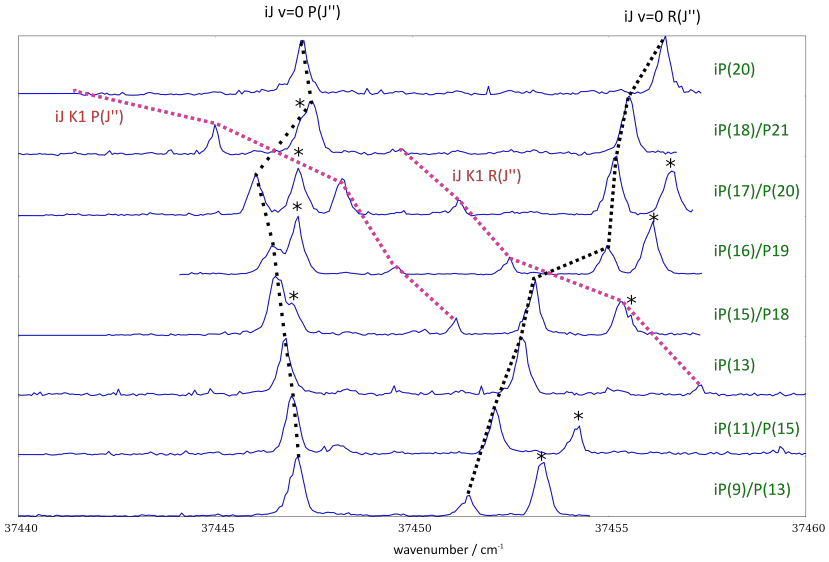

Figure 1: TC-RFWM spectra of $^{63}Cu^{65}Cu$ J-X (0-0). Single rotational lines where made visible by intermediate state labeling, pumping individual lines in the B-X (1-0) band (green labels). "i" indicates transitions in the $^{63}Cu^{65}Cu$ isotopologue, while the plain labels indicate overlapping transitions in the $^{63}Cu_2$ isotopologue. Spectral features contributed by the latter are marked with an asterisk. Within the rotational series that is pumped in $^{63}Cu^{65}Cu$, a not yet fully assigned perturbing state "K1" mixes with J, causing line shifts but also gains intensity itself.

[1] B. Visser et al., *J. Raman Spectrosc.*, **2016**, 47, 425-431.