Rydberg Excitons in Neutral Cuprite $(Cu_2O)_n$ Clusters, n < 13

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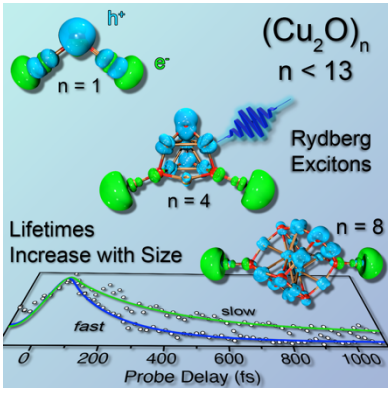
The ultrafast dynamics of sub-nanometer neutral cuprite clusters $(Cu_2O)_n$, n < 13, are examined with pump probe spectroscopy.[1] The addition and subtraction of each atom produce strong changes to both the cluster stability and excited state behavior, demonstrating the importance of stoichiometry.[2] Upon absorption of an ultraviolet (400 nm) photon, all clusters exhibit a sub-picosecond lifetime that we attribute to carrier recombination. Density functional theory shows a change in the structural motif between small planar clusters and three-dimensional structures at n = 4. This transition is accompanied by a change in the excited state relaxation behavior, marking the onset for which lifetimes increase gradually with size. Time-dependent density functional theory calculations show the excited state lifetimes align with calculated topological parameters and charge carrier delocalization associated with the formation of Rydberg excitons. Terminal Cu atoms are found to be important for the production of Rydberg excitons at the lowest optically allowed excited state. The electron centers on terminal Cu atoms and the hole becomes delocalized across the remainder of the cluster.



References

[1] C. H. Rotteger, C. K. Jarman, M. M. Sobol, S. F. Sutton and S. G. Sayres, Sub-picosecond Dynamics of Rydberg Excitons Produced from Ultraviolet Excitation of Neutral Cuprite (Cu2O)n Clusters, n < 13, *Under Review*, 2024, DOI:https://doi.org/10.26434/chemrxiv-2024-9cr26.

[2] C. H. Rotteger, C. K. Jarman, M. M. Sobol, S. F. Sutton and S. G. Sayres, Sub-Picosecond Photodynamics of small Neutral Copper Oxide Clusters, *Under Review*, 2024, DOI:10.26434/chemrxiv-2024-r3hbl.

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