Towards establishing the structure of liquid molecular transitions metal oxides through a joint experimental and computational investigation

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Molecular metal oxides stable under ambient conditions are exceptional in metal oxide chemistry. One of the best-known examples occurs for group 7 where M_2O_7 molecules exist for Mn, Tc, and Re. In the case of Tc, reactions of Tc_2O_7 and related species have been well-known to result in a red substance informally known as "technetium red" that has defied characterization efforts to date. We present a reexamination of the M_2O_7 class of molecular metal oxides from a joint computational and experimental approach. The M_2O_7 molecules offer some unusual chemistry, including three-center covalent bonding, negative thermal bond expansion, and (in the case of Re) a structure that is partially molecular and partially extended. Insights from our work on this family have led us to propose a likely model for "technetium red" based on an extensive computational investigation. Our model, which matches experiment closely, consists of a monomer with coordinatively unsaturated Tc sites which form strong and extensive interactions with adjacent molecules, predominantly involving Tc-Tc bonds, leading to a complex fluid.