

## METAL CLUSTERS

## Gold called to action



These spectra provide ideal benchmarks for quantum chemical calculations



Between mononuclear complexes and bulk metals exists a chemical space occupied by ligand-stabilized atomically precise metal clusters. To develop these clusters for optical and chemical applications we first need to understand their electronic structure — a challenge because of difficulties associated with synthesizing pure clusters and acquiring spectra at sufficient resolution. A team led by Christopher Johnson now finds that mass spectrometry can be used to separate clusters prior to and following irradiation, giving a detailed picture of how structure influences spectroscopy. They describe in *Angewandte Chemie International Edition* how the donicity of tertiary phosphine ligands bound to Au clusters can influence electronic structure as much as cluster nuclearity does.

The diversity of Au clusters stems not only from differences in their

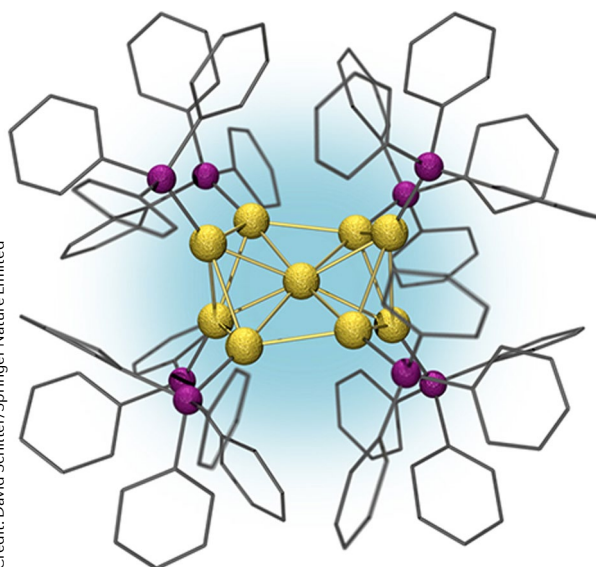
metal cores but also the ligands bound to their surfaces. It has so far proved difficult to exploit this diversity because clusters often form as mixtures. Indeed, when Johnson and colleagues reduced  $[\text{Au}(\text{PPh}_3)\text{Cl}]$  with  $\text{NaBH}_4$  they obtained both  $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$  and  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  as products. These well-known clusters are difficult to purify in the bulk, so the team instead subjected their solutions to electrospray ionization and separated the clusters in the gas phase, trapping the desired ions. The clusters were now too dilute for UV-visible spectrophotometry, and the team thus cooled the ion trap to  $\sim 4\text{ K}$ , a temperature at which  $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ , for example, binds He atoms through van der Waals interactions to afford  $\{[\text{Au}_8(\text{PPh}_3)_7]\cdot\text{He}_n\}^{2+}$ . When this cluster absorbs a photon of UV-visible light, the He atoms are liberated to give back the free cluster  $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$ , enabling the team to separate and quantify free and He-bound clusters using a mass analyser and detector. Measuring the fraction of free cluster as a function of wavelength is an indirect method to measure the absorption spectrum of the He-bound cluster, which is assumed to approximate the spectrum of the free cluster. This form of action spectroscopy, in which the ‘action’ is triggered by light, combines the high spectral resolution of low-temperature spectroscopy with the selectivity and sensitivity of mass spectrometry, but requires the team to generate extremely labile He-bound clusters. “It took us more than a year to optimize the instrument to achieve the needed signal-to-noise,” laments Johnson.

The absorption spectra of  $[\text{Au}_8(\text{PPh}_3)_7]^{2+}$  and  $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$  feature similar bands, and Johnson’s team assume these to arise from  $\pi \rightarrow \pi^*$ ,  $\text{Au}(d) \rightarrow \pi^*$ ,  $\text{Au}(s) \rightarrow \pi^*$  and  $\text{Au}(s) \rightarrow \text{Au}(s)$  electronic transitions, with the latter being lowest in energy. This qualitative similarity — the HOMO–LUMO gaps are coincident — is to be expected because the complexes differ only by a closed-shell  $\text{Au}(\text{PPh}_3)^+$  fragment that does not affect their delocalized electron counts. Although the superatom concept can be used to qualitatively explain the stability of certain metal cores, it cannot account for ligand effects on electronic structure. To study these effects, Johnson and co-workers measured spectra for octagold and nonagold complexes of tri(4-methylphenyl)phosphine and tri(4-methoxyphenyl)phosphine — ligands with greater donicity than  $\text{PPh}_3$ . Increasing the ligand donicity decreases the HOMO–LUMO gap of the corresponding complexes, an observation that goes against a common trend in coordination chemistry, in which stronger  $\sigma$ -donor ligands split metal valence  $d$  orbitals to a greater degree.

It is not yet obvious whether the principles of tuning electronic structure in the gas phase will be transferable to condensed phases. Moreover, the identities of the orbitals involved in the UV-visible absorptions remain unclear, but the high resolution of these data may help theoreticians decipher this problem. “These spectra provide ideal benchmarks for quantum chemical calculations,” concludes Johnson.

David Schilter

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