E.S.R. Spectrum of Matrix Isolated Au_3†

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The neutral gold cluster, Au_3, has been trapped in a benzene matrix at 77 K and its e.s.r. spectrum observed: it consists of sixteen sets of quartets with $a_{197}(2) = 382.9$ G (3.83×10^{-2} T), $a_{197}(1) = 58.0$ G (5.8×10^{-3} T), and $g = 1.865$; these parameters suggest a slightly bent structure with ${}^2B_2(C_{2v})$ ground state.

There is currently considerable interest in the preparation and characterization of small 'naked' metal clusters both in supersonic expansions and matrix isolation experiments.[1] However, experimental information on the properties of small clusters is limited. E.s.r. spectroscopy allows the geometry and electronic ground state of clusters containing at least one unpaired electron to be determined experimentally. We have previously obtained the e.s.r. spectra of the homonuclear group 1B trimers Ag_3 [2] and Cu_3,[3] produced by deposition of the respective metal atoms into a hydrocarbon matrix at

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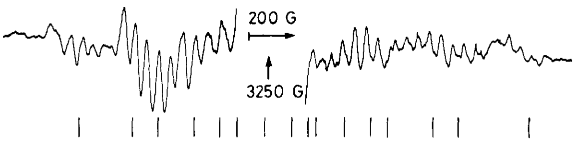

Figure 1. E.s.r. spectrum of Au_3 in perdeuteriobenzene, at 122 K, and an average microwave frequency of 9122.6 MHz. The stick diagram indicates the predicted line positions based on the e.s.r. parameters.

77 K using a rotating cryostat.[4] We report here the first identification by e.s.r. spectroscopy of a 'naked' gold cluster, the neutral triatomic, Au_3, and the characterization of this species as having an obtuse angled C_{2v} geometry and $^2B_2$ electronic ground state.

When gold atoms and perdeuteriobenzene were codeposited on the cold surface of a rotating cryostat the e.s.r. spectrum of the resulting sample, at 77 K, exhibited absorptions from four species: a Au–monobenzene complex previously reported;[4] two as yet unidentified products, the first with a_{Au} *ca.* 600 G‡ and marked anisotropy, the second a strong feature in the g *ca.* 2.000 region covering *ca.* 400 G; and a species with groups of absorptions over the field range 2100—4700 G which we assign to Au_3. Careful annealing of the sample in 10 K intervals to 190 K led to the complete decay of $Au(C_6D_6)$ at 140 K and Au atoms at 190 K leaving the central absorption and those from Au_3. Recooling the sample to 123 K gave the spectrum shown in Figure 1.

The spectrum arises from a single unpaired electron which shows equal, large, almost isotropic, hyperfine interaction with two equivalent Au atoms and a further, small interaction with a third Au atom. Sixteen groups of quartets are expected, resulting from second order effects, but only quartets from twelve groups are visible, four being obscured by the unassigned central feature. Analyses of the spectrum using an exact solution of the spin Hamiltonian[5] gave $g_{iso} = 1.865$, $a_{197}(2) = 382.9$ G (999.3 MHz). The average superhyperfine splitting of the quartets gave $a_{197}(1) = 58.0$ G. These parameters are consistent with a cluster of three gold atoms, entirely analogous to the Ag_3 and Cu_3 species reported earlier.

Using the appropriate one-electron parameter for Au[6] the isotropic hyperfine interactions in Au_3 give 6s unpaired spin populations of 0.42 for each of the terminal Au atoms and 0.06 for the central Au atom. These are very close to the equivalent populations observed in Ag_3 and CuAgCu.[7] The unpaired spin population on the central atom is probably negative and results from spin polarization effects. The deficiency in s spin population could be due to 6p and 5d orbital contributions to the SOMO which would not be detected because of the small anisotropic parameters for these orbitals in Au. The large negative isotropic g shift suggests that the unpaired electron acquires orbital angular momentum by coupling with a low-lying vacant orbital having p and/or d character. The larger g-shift compared with Ag_3 and Cu_3 is due mainly to the larger spin orbit coupling constant for Au but may also indicate a lower energy separation between ground and excited states for Au_3 and is good evidence that it is bent and not linear. Thus Au_3 has the same $^2B_2$ electronic ground state with C_{2v} symmetry as Ag_3 and Cu_3. This is contrary to theoretical calculations[8,9] which suggest an acute angled geometry, and also to the tentative conclusions from optical spectroscopy that Au_3 and Ag_3 have different electronic structures.[10]

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‡ 1 G = 10^{-4} T.

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