The E.S.R. Spectrum of $Ag(CO)_3$, a $^2A_1'$ Ground State Molecule

Carl A. Hampson,[a] James A. Howard,*[b] and Brynmor Mile*[a]

[a] *Department of Chemistry and Biochemistry, Liverpool Polytechnic, Byrom St., Liverpool L3 3AF, U.K.*
[b] *Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR9*

$Ag(CO)_3$ has been prepared by the reaction of carbon monoxide with silver atoms in a rotating cryostat at 77 K and its isotropic e.s.r. spectrum observed; in the case of $^{107}Ag(^{13}CO)_3$ in adamantane it consists of a doublet of quartets with $a_{107}(1) = -566.5$, $a_{13}(3) = -19.2$ G (1 G = 10^{-4} T), and $g = 2.00086$, which suggests a D_{3h} molecule with a $^2A_1'$ ground state and the unpaired electron located largely in the Ag 5s orbital.

Currently there is much interest in the interaction of carbon monoxide with metals because of the growing need to develop further the use of synthesis gas ($CO + H_2$) for producing basic petrochemical feedstocks.[1—4] We have recently reported[5] the anisotropic and isotropic e.s.r. spectra of $Cu(CO)_3$ which definitely show the molcule to be a planar trigonal π-radical with a $^2A_2''$ ground state in D_{3h} symmetry with the unpaired electron located almost entirely in the $4p_z$ orbital of the metal atom. Here we report the spectrum of $Ag(CO)_3$ which has a different electronic ground state ($^2A_1'$), with the free electron remaining in the 5s orbital of the silver atom.

The rotating cryostat technique has been described in detail elsewhere.[6,7] Ag atoms produced in a resistively heated molybdenum furnace were trapped on the freshly frozen surface of adamantane and bombarded with carbon monoxide. The products of reaction were immobilized in the interleaving spiral structure and after transfer from the cryostat, still at 77 K and under high vacuum, were examined by e.s.r. spectroscopy.

Figure 1(a) and (b) show the high and low field lines of the products of reaction of ^{107}Ag atoms with natural CO and ^{13}CO respectively (other lines in the central region are from Ag cluster/CO species and will be discussed elsewhere; lines labelled A are due to Ag atoms trapped in different matrix sites). The isotropic spectrum of $^{107}Ag(^{13}CO)_3$ is a doublet of

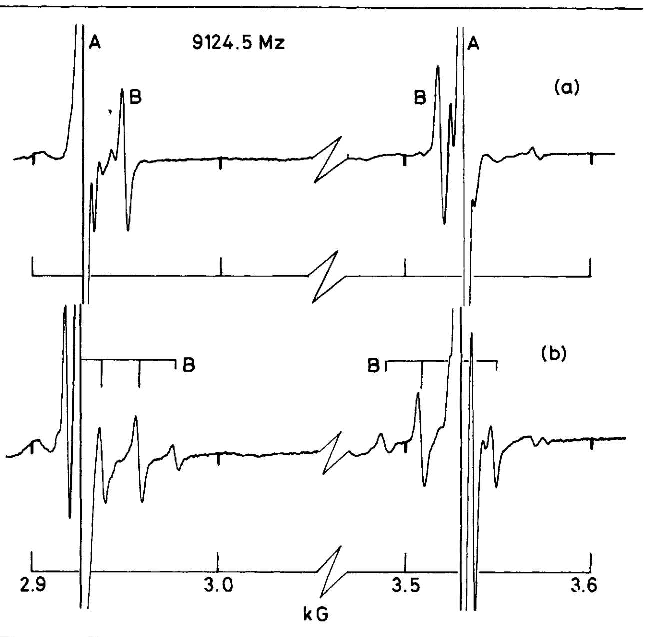

Figure 1. E.s.r. spectrum of tricarbonyl silver in adamantane at 98 K (a) $Ag(CO)_3$; (b) $Ag(^{13}CO)_3$.

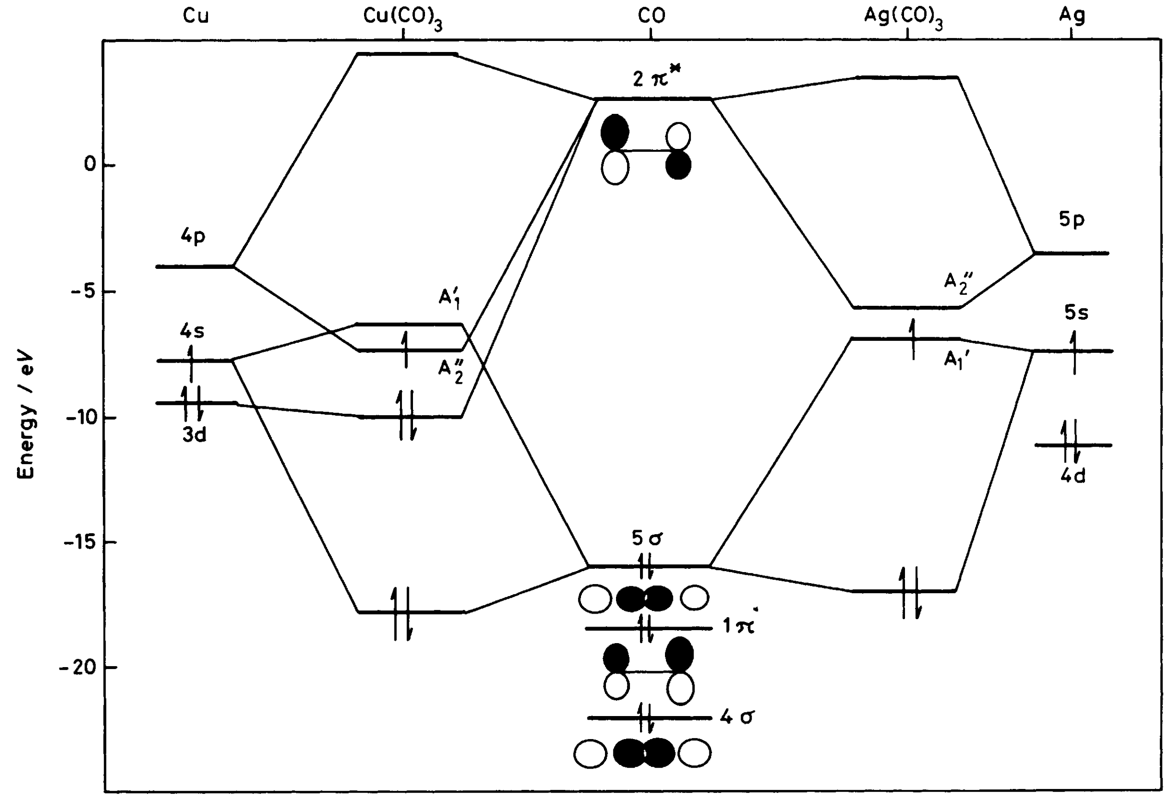

Figure 2. Qualitative molecular orbital energy level scheme for $Cu(CO)_3$ and $Ag(CO)_3$.

quartets (B) with the following parameters; $a_{107}(1) = -566.5$; $a_{13}(3) = -19.2$ G;† $g = 2.00086$. The corresponding parameters for natural ^{107}Ag(CO)$_3$ are, $a_{107} = -566.6$ G and $g = 2.00086$, showing clearly that the e.s.r. carrier contains one silver atom and three carbon monoxide molecules and is, therefore, Ag(CO)$_3$. Comparison with the one electron parameters for ^{107}Ag gives an unpaired spin population of 0.93 in the Ag 5s orbital[8] in sharp contrast to Cu(CO)$_3$ where the electron is located in the 4p$_z$ orbital.[5] The ^{13}C hyperfine interaction, hfi, of 19.3 G is also twice that in the tricarbonylcopper and is probably negative because of σ bond polarisation of carbon s orbital electrons. The large 5s character of the SOMO results in an isotropic spectrum even at 93 K compared with the anisotropic spectrum for Cu(CO)$_3$ which itself arises because of the p character of the SOMO.[5] Thus Ag(CO)$_3$ has a $^2A_1'$ ground electronic state in D_{3h} symmetry.

Our e.s.r. spectra are quite different from the anisotropic spectrum reported by Ozin and McIntosh in a CO matrix at 12 K which showed no silver hfi and was axially symmetric ($g_\parallel = 2.012$, $g_\perp = 1.995$).[9] These authors concluded that their spectrum for Ag(CO)$_3$ was consistent with that for Cu(CO)$_3$ and that both molecules had the same electronic ground state. Their spectrum is reminiscent of a peroxyl species and indeed we have observed such spectra when there were traces of oxygen in our carbonyl samples.‡

The marked difference between the Cu and Ag tricarbonyl species is unexpected and shows the subtle interplay of metal and ligand orbitals. A simplified energy level scheme is shown in Figure 2. In Cu(CO)$_3$ the energy of the 4s–5σ antibonding level is above that of the 4p$_z$–2π* bonding level so that promotion of the unpaired electron from the 4s to the 4p$_z$ orbital of Cu occurs. Such an inversion of metal energy levels does not occur in Ag(CO)$_3$. We suggest two possible reasons for this difference. One is that the Ag 5s orbital is further removed from the 5σ orbital than the 4s orbital of Cu (*ca.* 0.15 eV higher) so that the antibonding orbital level is raised less; also the 5p–2π* level does not fall below this orbital level because of the higher energy of the 5p orbital, though this is compensated to some extent by its closer proximity to the 2π* level. The other is that the $3d_{x^2-y^2}$, $3d_{xy}$, 2π* overlap aids bonding in Cu(CO)$_3$: INDO calculations show *ca.* 2% loss of 3d electrons from the Cu to the CO whereas the much lower lying 4d orbitals in Ag (*ca.* 2.8 eV below 5s) make a negligible contribution to bonding. This will result in a longer M–C bond and hence less perturbation of the metal s and p levels.

Although the differences in energy levels of Ag and Cu are small, the subtle effects noted here for the tricarbonyl species could be important in causing the greater efficiacy of Cu in catalytic processes such as the synthesis of methanol from CO and its oxidation to CO$_2$.

J. A. H. and B. M. thank NATO for a research grant and Drs. J. R. Morton, K. F. Preston, and J. S. Tse for many helpful discussions. C. A. H. wishes to acknowledge the award of an S.E.R.C. studentship.

Received, 22nd March 1985; Com. 386

References

1 M. E. Frank, *Chem. Teck.*, 1982, 358.
2 R. G. Pearson, *Inorg. Chem.*, 1984, **23**, 4675.
3 S. S. Sung and R. Hoffman, *J. Am. Chem. Soc.*, 1985, **107**, 578.
4 J. Pritchard and M. L. Sims, *Trans. Farad. Soc.*, 1963, **59**, 437; 1970, **66**, 427.
5 J. A. Howard, J. R. Morton, B. Mile, K. F. Preston, and R. Sutcliffe, *Chem. Phys. Lett.*, in the press.
6 J. E. Bennett, B. Mile, A. Thomas, and B. Ward, *Adv. Phys. Org. Chem.*, 1970, **8**, 1.
7 A. J. Buck, J. A. Howard, and B. Mile, *J. Am. Chem. Soc.*, 1983, **105**, 3381.
8 J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1978, **30**, 577.
9 D. McIntosh and G. A. Ozin, *J. Am. Chem. Soc.*, 1976, **98**, 3167.

---

† 1 G = 10^{-4} T

‡ *Added in proof*: Kasai and Jones (*J. Phys. Chem.*, 1985, **89**, 1147) have recently reported an e.s.r. spectrum of Ag(CO)$_3$ in argon at 4 K which is consistent with a $^2A_2''$ species analogous to Cu(CO)$_3$; it is possible that the Ag(CO)$_3$ we observe is not planar but is a pyramidal molecule in C_{3v} symmetry; this will be discussed in a full publication.