of these new materials that it is now possible to synthesize bimetallic complexes designed to take advantage of the properties of two different metal centers acting cooperatively. However, achieving the desired chemical reactivity from the bimetallic complexes has proven extremely difficult. These difficulties highlight our need to learn much more about the properties and reactions of metal–metal bonds. Our own goals of cleaving M–M' bonds with H_2 and of reducing CO with the resultant metal hydrides are unfulfilled. Nevertheless, our studies turned up new and interesting

chemistry of heterobimetallic complexes that have pointed the way to designing new molecules that may eventually lead to the desired reactivity.

Study of the Genesis, Structure, and Reactions of Small Metal Clusters Using a Rotating Cryostat[1]

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Investigations of metal clusters, both naked and ligated, are in vogue for two main reasons. First, they are now both theoretically and experimentally accessible, and second, they not only have an intrinsic scientific interest but also may have commercial applications in catalysis, material science, and electronics. The theorist has often led and spurred the experimentalist in this field as his ability to calculate and predict the geometries and electronic structures of such complex multielectron ensembles has grown.[2] Metal clusters are intermediate between the single-atom and the "infinite"-atom arrays of the bulk metal state and hence invoke questions about the number of atoms needed to produce the delocalized continuum electronic state of a metal. They are also probably the nuclei for phase changes, and silver clusters are the latent image of the silver halide photographic process.[3,4] They are neither "fish nor fowl", and in many ways it is their dissimilarity to both the extreme atomic and metallic states that provides their fascination for the chemist and is the reason for their importance in so many physicochemical processes.

In this review we shall deal only with naked neutral metal clusters, since several reviews on carbonyl and other clusters are already available.[5] Ligand-free metal clusters have also been recently reviewed by Ozin and Mitchell,[6] Weltner and Van Zee,[7] and Morse.[8]

Two experimental methods have been used to prepare naked metal clusters:

(I) Pulsed laser ablation of bulk metal and expansion cooling has been used to produce gaseous clusters whose structures and reactions are studied by multiphoton laser mass spectroscopy and other techniques.[9-12]

(II) Matrix isolation methods in conjunction with high-temperature sources of metal atoms and clusters is a further extension of the isolation methods used so successfully to study transient free-radical species.[13-15]

The laser ablation method has recently provided penetrating insight into metal clusters and their reactions, but in this review we will concentrate on results from matrix isolation methods, especially on our own work using the rotating cryostat variant of the technique.

Matrix Isolation. Active species of interest are kept in isolation by being trapped in substitutional and interstitial sites in a solid matrix, usually at low temperatures. The low diffusion rate in the solid effectively

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Figure 1. Reaction surface of the rotating cryostat.

Figure 2. Correlation diagram linking the level structures of linear, obtuse, equilateral, and actute triangular trimer, M_3, constructed from atoms with one unpaired s electron.
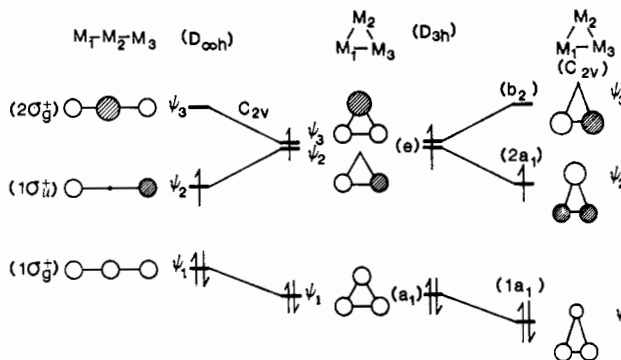
eliminates bimolecular reactions between the species. Thus, they can persist in this trapped metastable state for a long time and can be examined at leisure by the full range of spectroscopic techniques. In some cases the reactions of the species with other substrates also trapped in the matrix can be followed usually during annealing of the samples. We have used almost exclusively electron paramagnetic resonance (EPR) spectroscopy in our studies using the rotating cryostat.

Principle of the Rotating Cryostat.[16,17] This technique is essentially a molecular engineering device for the controlled, intimate mixing of normally immiscible materials at the molecular level. A stainless steel drum (o.d. = 12 cm) containing liquid nitrogen spins at high speed ($\sim$2000 rpm) in an evacuated chamber ($<10^{-6}$ Torr), and vapors of the inert matrix, metal, and in some cases another metal or reactant are deposited in sequence from jets positioned a few millimeters away from the moving perimeter of the drum (Figure 1). The metal vapors, which are generally monovalent,[18] are generated either in resistively heated molybdenum pouch furnaces or tungsten coils to temperatures in the range 800–2400 °C.[19] Usually, about 10 monolayers of the matrix, 0.1–0.01 monolayers of metal, and other reactants are deposited per revolution of the drum. The interleaving spirals of each material build up to a deposit ca. 2 mm thick and $\sim$1 cm wide which can be examined in situ by reflectance IR and UV–visible spectroscopy or by EPR spectroscopy after transfer of the deposit, still at 77 K and under high vacuum, to tubes suitable for insertion into the spectrometer cavity. The distinct spatial and temporal separation of the deposition of each component appears to have definite advantages in the study of metal clusters since few of these clusters have been found in inert gas matrices by using the more conventional codeposition approach. We have made extensive use of inert hydrocarbon matrices, especially the "plastic solid" adamantane which has cavities of 5–6 Å in dimension

and which allows the species to be trapped and observed at much higher temperatures than in inert gas matrices. This can be extremely useful since isotropic or liquid-phase-like spectra sometimes result. We have found no evidence of reaction of metal atoms or clusters with the hydrocarbon matrices and little effect of the matrix on spectra; we regard the matrices as inert, and they probably perturb the guest no more than inert gas matrices where the cavities are smaller.

We have prepared a variety of trimers, pentamers, and septamers from groups 1, 11, and 13; these clusters are discussed separately in the following sections.

Trimers. To date, we have successfully prepared and identified six trimers constructed from atoms with one valence s electron: Li_3[20] and Na_3[21] from group 1 and Cu_3,[22] Ag_3,[23] Au_3,[24] and the heteronuclear trimer Cu_2Ag[25] from group 11. There is controversy over the structure of these trimers, and it is useful to consider the molecular orbitals that can be constructed from a single s orbital on each center (Figure 2).

The odd electron cannot occupy an e orbital in an equilateral triangular geometry because according to the Jahn–Teller theorem[26] this state must distort to either an A_1 or a B_2 state with C_{2v} symmetry or to a linear $D_{\infty h}$ structure. Consequently, the unpaired electron can occupy either a σ_u^+ orbital with linear geometry, a b_2 orbital with obtuse triangular geometry, or an a_1 orbital with acute triangular geometry. Most of the unpaired s spin population will reside on the two terminal atoms in the linear and obtuse triangular geometries and on the central atom in the acute triangular geometry.

Li_3 is readily prepared from Li atoms in adamantane,[20] and it has three magnetically equivalent Li nuclei in the temperature range 4–300 K with $a_7(3)$ = 92.7 MHz and g = 2.001. These parameters are almost identical with those obtained by Garland and Lindsay[27]

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for Li_3 prepared by photolysis of Li atoms in argon, indicating that this trimer has the same structure in these very different matrices. Three magnetically equivalent nuclei suggests that, even at 4 K, Li_3 is a fluxional molecule in which the three possible stationary configurations exist in shallow minima on the potential energy surface and pseudorotation occurs at temperatures >4 K either because of tunneling between adjacent wells or because of a low-energy barrier to pseudorotation. Ab initio calculations[28] on Li_3 suggest that the $^2B_2$ state has the lowest energy of the C_{2v} structures and that the $^2A_1$ state, through which pseudorotation occurs, is at a saddle point on the energy barrier. The total s spin character of the singly occupied molecular orbital of Li_3 ($\sum \rho_s$) is obtained by comparison of the isotropic hyperfine interaction (hfi) a with the value of the atomic parameter $A = (8\pi/3)g\beta\gamma\Psi^2(O)$ for the valence s shell of Li,[29] i.e., $\sum \rho_s = 3a/A$. This calculation gives $\sum \rho_s = 0.70$, which means that the SOMO must have ~30% 2p character. This latter value cannot be confirmed by comparing the dipolar hyperfine interaction with the atomic parameter $P = \alpha g\beta\gamma\langle r^{-3}\rangle$ for the valence p shell of Li[29] because the spectrum of Li_3 did not show anisotropy even at 4 K, probably because of the small value of P. It is worth noting that formation of Li_3 in argon[27] requires photolysis of the matrix doped with Li while Li_3 is formed in adamantane at 77 K without photolysis. This is probably because Li atoms are more mobile on the hydrocarbon surface at the higher temperature.

Moskovits and Mejean,[30] from a laser-induced resonance fluorescence study, have proposed that Li_3 is pseudorotating in argon and in one site in xenon but in krypton and in a second site in xenon it has a rigid acute triangular ($^2A_1$) geometry. Unfortunately, these observations have not been confirmed by EPR spectroscopy although Garland and Lindsay[27] do imply formation of transient ($^2B_2$) Li_3 with $a(2) = 46.1$ G, $a(1) = \pm 6.8$ G, and $g = 2.0047$, but this observation has not been confirmed.

Na_3 has been prepared in adamantane[20] and from 4 to 170 K has three magnetically equivalent nuclei with the magnetic parameters $a_{23}(3) = 93.6$ G and $g = 2.0027$, values that are similar to those for pseudorotating Na_3 in three sites in argon[31] ($a_{23}(3) = 93.2$–94.7 G and $g = 2.0012$–2.0018). There are, however, two major and important differences between the spectra in the two matrices. First, in argon only the $M_I = \pm^9/_2$ and $\pm^3/_2$ transitions are observed, the other transitions being broadened by the switching between the three $^2B_2$ forms which though of identical energy have a different M_I value at one of the three Na nuclei. In adamantane all transitions are seen, and the $M_I = \pm^7/_2$, $\pm^5/_2$, and $\pm^1/_2$ lines are not appreciably broadened and have the intensities expected for a "normal" spectrum. Second, there is no detectable dynamic frequency shift in adamantane whereas a shift of 5–10 G was observed in argon. Both these differences are explicable if the residence time for each $^2B_2$ state in its shallow potential well, τ_c, in adamantane is 1/10 the value it is in argon.

All three homonuclear group 11 trimers and one heteronuclear trimer Cu_2Ag have been prepared, and they have most of the unpaired ns spin population on the two terminal atoms, indicating either a linear or obtuse triangular geometry. The values of $\sum \rho_s$ for the four trimers are 0.6 (Cu_3), 0.88 (Ag_3), 0.84 (Au_3), and 0.82 ($CuAgCu$). These values indicate a small amount of p and/or d character in the SOMO of Ag_3, Au_3, and the mixed trimer and a substantial contribution to the SOMO of Cu_3. This is probably associated with the smaller energy difference between the 3d and 4s orbitals of Cu compared with the $(n-1)$d and ns orbital separation of Ag and Au although a larger d orbital contribution is only consistent with the g value of 1.9925 for Cu_3 if some 4p orbital participation is also involved. It is interesting to note that the central Ag atom substantially reduces the s/p–d orbital character of the SOMO in CuAgCu probably because it "insulates" the d levels of the two terminal Cu nuclei from each other.

Although it is not possible to distinguish between linear and obtuse triangular geometries from metal hyperfine interactions, our analysis of the spectrum of Ag_3 in terms of an orthorhombic $\mathbf{g}$ tensor having all three principal values less than the free-spin value of 2.0023 suggests that Ag_3 is bent with a $^2B_2$ ground state since a linear species would have an axial $\mathbf{g}$ tensor with $g_\parallel$ close to 2.0023. Cu_3, Au_3, and Cu_2Ag all have g factors below 2.0023 and are thought to be isostructural with Ag_3.

Cu_3 and Ag_3 have recently been observed by EPR in solid N_2[32,33] but occur in the acute triangular form in this matrix. Formation of obtuse forms in hydrocarbons and acute forms in nitrogen is puzzling, but the two states do lie close in energy ($\Delta E \sim 0.14$ eV) and the two matrices may differentiate the two shallow minima in the broad potential well; i.e., the difference arises because of matrix perturbation effects. However, it is also possible that the N_2 acts as a ligand and stabilizes the acute form at the expense of the obtuse form.

Although none of the group 11 trimers have been detected in rare gas matrices by EPR, itself a mystery, there are several reports of their detection by other spectroscopic techniques, most notably laser Raman and UV–visible spectroscopy. For instance, DiLella, Taylor, and Moskovits[34] have assigned a resonance Raman spectrum to Cu_3 trapped in argon and have concluded that it is a fluxional Jahn–Teller molecule with no barrier to pseudorotation. On the other hand, Rohlfing and Valenti[35] have shown from a laser-excited fluorescence spectroscopic study of jet-cooled Cu_3 that the barrier to pseudorotation is not negligible. The electronically excited $^2E''$ state is, however, a fluxional molecule which freely rotates even in the lowest vibronic level as suggested by Moskovits.

UV–visible spectra of Cu_3[36] and Ag_3[37] in rare gas matrices have been reported and it has been suggested

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that three isomers of Ag_3 can coexist in Xe and Kr matrices. Furthermore, it would appear that these species can be reversibly transformed into one another by direct laser excitation.[37] We eagerly await confirmation of these interesting observations by EPR spectroscopy.

There have been a variety of theoretical calculations on group 11 trimers. Two of the most recent are those of Wang[38] on Cu_3, who calculated that the $^2A_1$ state has the lowest energy, and Basch[39] on Ag_3, who concluded from an ab initio relativistic ECP–SCF and CI study that the $^2E'$ state distorts to give a slightly bent $^2B_2$ ground state with a very shallow bending mode potential surface and that the $^2A_1$ state is 0.14 eV above the $^2B_2$ state. Our EPR results on these two trimers clearly favor Basch's calculations rather than those of Wang. Langhoff, Bauschicher, Walch, and Laskowski[40,41] using refined SCF methods have recently calculated a $^2B_2$ ground state for Cu_3 and Ag_3, in agreement with our experiments, but predict that CuAgCu should have a $^2A_1$ ground state, in contradiction to our results. Interestingly, they find extensive d-orbital participation in Cu_3 and negligible participation in Ag_3, in agreement with our work.

Two trimers have been prepared from atoms with the odd electron in a p orbital, Al_3[42] and Ga_3.[43] Al_3 at temperatures down to 4 K has an almost isotropic EPR spectrum with $a_{\parallel}$ = 100 MHz, $a_{\perp}$ = 119 MHz, $g_{\parallel}$ = 1.9941, and $g_{\perp}$ = 1.9935, values which can be compared to those for an Al atom in argon at 4.2 K ($a_{\parallel}$ = 142.8 MHz and $a_{\perp}$ = -98.7 MHz). The total unpaired spin population is therefore too large for a doublet ground state, and we have concluded that Al_3 has a quartet $^4A_2$ ground state. This is only consistent with an isotropic spectrum if one-third of the spin population is located in each of the three p orbitals on each Al nucleus, i.e., similar to the ^4S state of the nitrogen atom.[44]

This assignment has, however, not been confirmed by the observation of transitions corresponding to zero-field splitting and to changes of greater than unity in the electron spin projection ($\Delta M_s > \pm 1$). We did, however, find that the Q-band spectrum was better resolved than the X-band spectrum, which is more consistent with a quartet than a doublet ground state. In contrast to our work, a recent molecular beam estimate of the magnetic moment of Al_3 by magnetic deflection measurements suggests a doublet ground state.[45] A doublet ground state has received support from a total-energy calculation for almost equilateral triangular Al_3 by Upton,[46] whereas an earlier calculation by Paccioni and Koutecky[47] favors a quartet ground state. The most recent ab initio calculations by Tse[48]

give four electronic states, $^2A_1$, $^4A_2$, $^4B_1$, and $^2B_1$, lying within 6 kcal mol^{-1} of each other with the $^2A_1$ state only 2.74 kcal mol^{-1} more stable than the $^4A_2$ state. However, as Tse points out, the present level of theoretical treatment cannot provide a definitive assignment to the true ground state of Al_3 without full geometric optimization and energy calculations at the MRCI level.

$^{69}Ga_3$ has recently been prepared in our laboratory from ^{69}Ga atoms in adamantane. It has three magnetically equivalent nuclei with $a_{69}(3)$ = 237.6 MHz and g = 1.9672[43] and appears to have the same structure and ground state as Al_3.

Pentamers. The only pentamers that have been prepared and identified in inert hydrocarbon matrices are the homonuclear pentamers Cu_5[49] and Ag_5[50] and the heteronuclear pentamers $CuAg_4$ and Cu_2Ag_3.[51] Interstingly, not one of the group 1 pentamers has yet been detected by EPR in inert gas matrices and high-spin (S = 25/2) Mn_5[52] is the only other pentamer that has been identified by this technique.

The group 11 pentamers have all been prepared by photolysis of the atoms during deposition, although Ag_5 can be prepared by annealing Ag atoms in adamantane to 223 K. Ag_5 would appear to be EPR silent at this temperature and is only visible on recooling to 77 K. EPR spectra of Cu_5, Ag_5, $CuAg_4$, and Cu_2Ag_3 have been interpreted in terms of S = $^1/_2$ molecules with most of the unpaired s spin population located on two nuclei. Comparison of hfi with values of A gave $\sum\rho_{4s}(Cu_5)$ = 0.56, $\sum\rho_{5s}(Ag_5)$ = 0.62, $\sum\rho_s(CuAg_5)$ = 0.6, and $\sum\rho_s(Cu_2Ag_3)$ = 0.58. Thus, Cu_5 has a total s spin population similar to that for Cu_3 while Ag_5 and the heteronuclear pentamers have significantly less s spin population than Ag_3 and Cu_2Ag.

A variety of structures are possible for an ensemble of five atoms including linear, trigonal bipyramid, square pyramid, body-centered square, and pentagon, but EPR data are only consistent with a distorted trigonal bipyramid. Thus, semiempirical INDO/2 calculations on the D_{3h} arrangement of Cu atoms locates the unpaired electron in an e' orbital formed by the linear combination of the equatorial Cu orbitals. A symmetric (D_{3h}) trigonal bipyramid must undergo Jahn–Teller distortion to either a B_2 or an A_1 state with C_{2v} symmetry. The B_2 state, where the equatorial triangle has become obtuse, has most of the unpaired s spin population on two equatorial nuclei and the A_1 state, where the triangle has become acute, has an unpaired s spin distribution that favors one equatorial nucleus. Magnetic data for Cu_5 and Ag_5 and by analogy $CuAg_4$ and Cu_2Ag_3 favor a $^2B_2$ ground electronic state for homo- and heteronuclear group 11 pentamers.

Our suggestion that the Jahn–Teller theorem requires the pentamers to distort from D_{3h} symmetry has recently been questioned for Ag_5 by theoretical Dirac scattered-wave calculations which indicate that spin-orbit interaction removes $^2E'$ orbital degeneracy and hence obviates the necessity for distortion to C_{2v} symmetry.[53] The calculated Ag hfi were in better agree-

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ment with experimental values for D_{3h} than C_{2v} symmetry. Calculated and empirical estimates of the Fermi contact term were in good agreement, and both assignments agree that this is the major contribution to the observed hyperfine tensors.

Septamers. Li_7 is the only septamer that we have prepared, and it is formed alongside Li_3 in adamantane at high fluxes of Li atoms. The EPR parameters in the inert hydrocarbon matrix are $a_7(2) = 36.4$ G, $a_7(5) \sim 2$ G, and $g = 2.00045$, parameters that are similar to those for Li_7 in argon.[54] Li_7 must, therefore, have the same pentagonal-bipyramid structure, electronic ground-state distribution of the unpaired spin, and s–p ratio in the SOMO state in hydrocarbon and rare gas matrices. Lindsay and co-workers[55] assign similar structures to Na_7 and K_7 from their EPR spectra which also have large unpaired spin populations on two nuclei and small populations on the other five nuclei.

Weltner[56] has very recently reported the EPR spectrum of Ag_7 in neon. This cluster has the tentative parameters $a_{107}^{\perp}(2) = 204$ G, $a_{107}(5) = 7.4$ G, and $g_{\perp} = 2.095$, values that are close enough to our values for Ag_5 in c-C_6D_{12} for Weltner to suggest that we had prepared the septamer rather than the pentamer. Unfortunately, our spectrum was not as well-resolved as Weltner's and there could be some ambiguity in our assignment. We do, however, have good evidence that Ag_5 is indeed formed in adamantane from the observation of better resolved EPR spectrum of the $Ag_5[C_2H_4]$ complex when the clusters are reacted with ethylene. It is likely that the magnetic parameters of pentagonal-bipyramidal Ag_7 will be similar to those for trigonal-bipyramidal Ag_5 so that the similarity in itself does not constitute conclusive evidence for the absence of Ag_5 in adamantane.

Sc_{13}. This is the largest cluster yet detected by EPR, and it is believed to have a icosahedron structure and a ^2A_g ground state with the unpaired spin located on at least nine equivalent nuclei. It could, however, be a dynamic Jahn–Teller molecule with only a small barrier between distorted conformations.[57]

Clusters, Molecules, or Metals. No concensus exists as to how "many atoms maketh metal", the answer itself depending on which property of the metal is being addressed. As the metal particle size diminishes until its dimensions become comparable to the wavelength of the Fermi electron, the separation between electronic levels, Δ, increases ($\Delta = \eta/N$, where η is the Fermi potential and N is the number of atoms in the particle) until "quantum size effects" manifest themselves as marked departures from the bulk metal of such properties as magnetic susceptibility and conduction electron spin resonance (CESR).[58] There are clear indications of such effects experimentally.[58] At still lower particle sizes the additional effect of decoupling s, p, and d orbitals occurs until the separate orbitals of the isolated metal atom are attained. Theoretical predictions of the number of atoms, n, needed

for such s, p, and d overlap depend on the approximations used. For instance, for Cu values of n greater than 13 are indicated by extended Hartree–Fock calculations (EHF),[59,60] but SCF–$X\alpha$ calculations[61,62] show its onset even at $n = 3$. There is a dearth of experimental information on this aspect.

The experimental s character of the SOMO for alkali metals (Lindsay and co-workers) and transition metals (our results) are listed in Table I, which also includes the values for an electron on the Fermi surface of the bulk metal. These results are more in accord with the predictions of the SCF–$X\alpha$ rather than the EHF calculations since they show a progressive loss of s character in the SOMO even for clusters of 3–5 atoms. The loss of s character in the transition-metal clusters is related to the ns–$(n-1)d$ orbital separation in the atom (1.38, 3.74, and 1.13 eV for Cu, Ag, and Au, respectively), indicating the importance of s–d overlap rather than s–p overlap; the "insulating" effect of the central Ag atom in CuAgCu also supports this conclusion. There is no apparent rationale for the trends in the alkali-metal trimers. Although we can only characterize the highest orbital by EPR, similar s–d overlap can be inferred in the lower fully occupied orbitals of the clusters. However, complete delocalization of the electron has clearly not occurred at these cluster sizes, and indeed one of the most striking general features is the concentration of spin at two atoms in the trimers, pentamers, and septamers; i.e., these clusters are molecular, not metallic. The localization of the free electron at two positions has important consequences for the reactions of clusters, which we will now discuss.

Reactions of Metal Clusters. Again we have the two extremes of reaction conditions, at the surface of a bulk solid and with single atoms, the former now being studied with the powerful new tools of surface science[64] and the latter the subject of research over decades. Understanding of heterogeneous catalysts is still at a fairly primitive level compared with that of homogeneous reactions, and the huge computational requirements limit theoretical calculations of even the starting reactants let alone the reaction pathways. Hence, we are obliged to model and mimic by studying

Table I.
s Character of the SOMO of Alkali-Metal and Coinage Clusters, M_n, and the Fermi Surface of the Bulk Metal[a]

metal	$n = 2$[b]	$n = 3$	$n = 5$	$n = 7$	$n \rightarrow \alpha$ bulk metal
Li[a]	0.86	0.68		0.43	0.42
Na[a]	0.93	0.87		0.64	0.66
K[a]	0.94	0.89		0.63	0.66
Cu		0.63	0.64		0.49
Ag		0.94	0.64		0.60
Au		0.84			0.71

[a] See ref 27 for details of the Fermi surface calculation. [b] Calculated values from ref 63.

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these reactons on smaller clusters like those discussed in this review. Rooney[65] has recently suggested that many catalyst reactions occur essentially at single metal atoms or ions and that the extended array of metal atoms is needed mainly to generate and stabilize these individual atom or ion sites. Thus, reactions on small metal clusters may well provide realistic models for heterogeneous catalysis at active sites. Studies of such reactions in the gas phase are proceeding apace, and unexpected periodicities and aperiodicities and discontinuities at certain cluster sizes are being revealed.[66-68]

Reactions with Molecular Oxygen. Oxygen is one of the simplest adsorbates, and heterogeneous oxidations of great technical importance are the epoxidation of ethylene and the oxidation of alkenes and alcohols.[69,70] However, doubt and controversy still surround the nature of the active oxygen in such reactions.[71-73] We have found marked differences between Cu clusters and Al clusters in their reactions with O_2 at 77 K. For copper almost complete electron transfer occurs to give $Cu_3^+O_2^-$ and $Cu_5^+O_2^-$, which have high g values ($g_\parallel = 2.261$) and a small equal 4s (~ 0.05) unpaired spin population on the three and five copper atoms of the metal partners of the tight ion pair.[74] The bonding results from one-electron transfer to the $1\pi_g^*$ antibonding orbital of O_2 and a small back-donation of electrons from the O_2 $1\pi_u$ bonding orbitals to orbitals of correct symmetry in the cluster. The equivalence of the copper atoms contrasts with their nonequivalence in the parent cluster and illustrates the significant electronic and geometric structural changes of the metal atoms within the cluster that accompany cluster substrate reaction. Probably such changes also occur at the active sites in heterogeneous catalysis; i.e., the catalytic ensemble of atoms is flexible and changes shape during the catalytic event.

The reaction of Al_3 with oxygen does not result in charge-transfer reactions but produces a species whose EPR parameters ($g_\parallel = 2.023$, $g_\perp = 2.006$)[75] are more consistent with a peroxyl, Al_3O_2, similar to other peroxyls, e.g., RO_2[76] and CuO_2.[77] A doublet or sextet ground state is possible for this reaction between the quartet Al_3 and the triplet O_2 molecules, but the EPR spectrum suggests a doublet state. The equivalence of the aluminum atoms ($a_{Al} = 5.4$ G) and the 90% drop in unpaired spin population suggest that an O_2 molecule

lies with the O–O bond along the C_{3v} axis of the triangular Al_3 cluster although a fluxional molecule with the O_2 switching between alternate pairs of aluminum atoms cannot be ruled out.

Gas-phase studies show that Al_3 clusters do not react with oxygen to form stable products, but this is not incompatible with our results since the time scales for reaction are so different (~ 10 ns in the gas phase).[66]

Reactions with Carbon Monoxide. Because catalytic reactions of CO are of industrial importance,[78] there have been extensive studies of CO adsorbed on metal surfaces which have revealed a range of bound states from perpendicular (end-on) bonding to a single metal atom, bridged bonding to two and more surface atoms and sideways bonding with the CO lying parallel to the surface and bound to two metal atoms.

Recent studies of reaction of CO with silver on the rotating cryostat[79] have tentatively shown that two silver cluster complexes are formed which we tentatively assign to $Ag_5(CO)_x$ and $Ag_{13}(CO)_x$. The Ag_5 framework in Ag_5CO has a similar structure to that in naked Ag_5, but the spin density on the metal cluster in Ag_5CO is 15% less and the g factors are significantly smaller ($\Delta g_\perp = -0.09$ and $\Delta g_\parallel = -0.007$), implying less correlation of the SOMO with filled orbitals in the cluster carbonyl.

Reactions with Alkenes. Alkenes are major building blocks of the petrochemical industry,[80] but although their numerous catalytic reactions have been studied extensively, understanding still remains at a qualitative level.

The reaction of ethylene with silver clusters on the rotating cyrostat gives a cluster ethylene complex $Ag_5[C_2H_4]_x$, with a large hyperfine interaction of 200 MHz with two Ag nuclei but an equal interaction with the remaining three Ag nuclei showing that a small structural rearrangement of the Ag_5 framework has occurred.

Studies of the reactions of CO and alkenes are still at an early stage and only tentative conclusions can be drawn, but even the occurrence of cluster reactions at 77 K is of interest in the context of heterogeneous catalysis since it implies activation energy barriers of less than 20 kJ mol^{-1}.

Catalytic Implications. There are two important interrelated aspects. First, both experiment and theory show that clusters have several shapes with similar energies and that each structure has a large number of close-lying electronic states. Second, because of these features, clusters are flexible and can adapt geometrically and electronically to accommodate an approaching reactant molecule and then reassemble back to the original state as that molecule or a changed molecule leaves the cluster. Perhaps this flexibility and accommodation is one of the essential features of active catalytic sites even in supported metal catalysts. The term site dynamics has been coined for these features, and it is of some interest that it can be observed so directly in matrix studies of cluster reactions.

Future Developments. The area of naked metal clusters is most notable for the sparsity of information and understanding about the clusters of most metals,

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so that there is considerable scope for advances by both experimentalists and theoreticians. The development of monodisperse sources of single well-defined metal clusters is being actively persued by numerous groups worldwide, and the eventual availability of such sources together with the use of many rather than just one spectroscopic technique will allow their geometrics, electronic structures, and reactions to be determined without equivocation. There are distinct commercial applications for clusters and small particles as evidenced

by the production of ~10 kg per month of such materials for commercial evaluation.[82]

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Energy Redistribution in Unimolecular Ion Dissociations

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Introduction

Observation of unimolecular dissociations of gas-phase ions will be familiar to anyone who has had occasion to examine fragmentation patterns in mass spectra. The fundamental significance of these molecular ion dissociations has long been recognized and investigated. In principle, such dissociations are no different than those of neutral species, yet quite apart from their intrinsic interest ions hold special attractions when we wish to investigate elementary reaction processes. Prominent among these is that for bound electronic states the intermolecular potential at long range is frequently dominated by well-understood electrostatic forces. Even in the absence of specific information, we thus can start with a plausible working model for the long-range interaction potential. More pragmatically, we can note the experimental convenience which arises from the interaction of charged particles with electrostatic and magnetic fields. This permits efficient detection of individual ions and the use of some otherwise novel techniques. Mass spectrometry is of course one such example. Another more specialized example is photoelectron–photoion coincidence (PEPICO) detection of ions. Quite generally, PEPICO techniques allow the preparation and observation of energy-selected and, indeed, state-selected ions.

The central role of reactant energy gives us a paradigm for the understanding of elementary reactions. As a molecule dissociates, the configuration of its constituent parts (nucleii plus electrons) changes: this is reflected in changes of the potential energy and the disposition of nonpotential energy (vibrations, etc.). Following the evolution of the energy distribution through a reaction is ideally tantamount to following the rearrangement of the individual atoms. While this

remains an unrealized goal, we can at least seek to examine the energy redistribution apparent in the products coming from an initially state-selected reactant. As will be seen, this is a realistic option with PEPICO experiments where translational energy distributions can be readily obtained.

Perhaps the reader will find the probing of dissociation lifetimes (i.e., rates) a more familiar tactic for the characterization of dissociation mechanisms. In principle, both the lifetime and energy distributions will depend on the detailed dynamics of dissociation, but in practice these two types of data can be complementary. This is most clearly seen in the context of those many reaction theories which postulate a transition state or critical region of system phase space through which the system passes as it evolves from reactants to products.[1-3] In such cases the transition state represents a point of no return, and the lifetime is therefore assumed to be determined prior to this point. Interactions among the various degrees of freedom, affecting the observed final energy distribution of the products, can, however, persist to greater separations. In extremis one can argue that product lifetime distributions are determined by short-range dynamics whereas product energy distributions reflect the long-range dynamics of the system. While such statements may be somewhat lacking in rigor, they nevertheless appear to have a degree of validity, certainly for some types of unimolecular ion dissociation.[4]

The following Account considers some of these issues by using results obtained for energy redistribution in the dissociation of moderate sized ions.

The PEPICO Technique

PEPICO methods were first introduced by Brehm[5] and in slightly more versatile form by Eland and co-workers.[6] There now exist two major variants of the

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