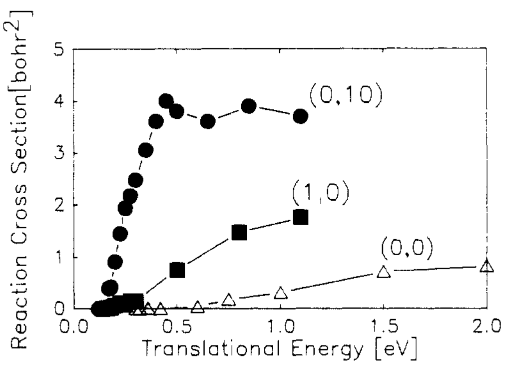

Figure 2. Reaction cross section for hydrogen atom transfer as a function of translational energy out of specific HB vibrotational states, (v,J). The potential energy surface is thermoneutral.

energy was taken as the zero-point energy of the diatomic molecule. When either rotational or vibrational energy was being varied, the collision (translational) energy was 0.5 eV (48 kJ mol^{-1}). This admittedly high energy was chosen to ensure good statistics, but the results are typical of all energies above the reaction threshold. This is illustrated by the data of Figure 2, in which the translational energy dependence of the cross section for fixed internal vibrational and rotational energy is shown.

It is clear from both Figures 1 and 2 that reactant rotation is more effective at promoting a light-atom-transfer reaction than either translation or vibration, regardless of the reaction exoergicity and the total energy. This finding is confirmed by calculations of other workers,[10,14,15] although this point is not explicitly mentioned in their papers. One apparent counterexample has been reported for $O + HCl \rightarrow OH + Cl$ by Persky and Broida.[24] On their surface II, they see a decline in reactivity with rotation. However, their rotational energy was always less than 0.5 eV. For higher rotational energy, and at higher translational energies, rotation strongly enhanced H atom transfer.[25] A recent landmark state-to-state experiment[26] which found rotational enhancement of reaction was also a light-atom-transfer reaction. Using the data of Figure 2, we can calculate[27] thermal rate constants for reaction for each case. These are $k(v{=}0,J{=}0) = 6.6 \times 10^5$, $k(1,0) = 7.4 \times 10^8$, and $k(0,10) = 1.4 \times 10^{10}$ cm^3 mol^{-1} s^{-1} (±10%) at 300 K. Therefore, while vibration enhances the rate constant by 3 orders of magnitude, the same energy in rotation enhances it by more than 4. It appears that rotational excitation is the most efficient way to promote hydrogen atom abstraction.

We have, as yet, no conclusive explanation for this phenomenon. One suggestion[11] is that, as a light atom is transferred, the bond under attack stretches rapidly, strongly coupling rotational and over-the-barrier motion. Another view[10,15] is that the mass combination may allow free "figure-of-eight" motion of the H around the heavier atoms.

These results, of course, have only been shown to hold for atom + diatom reactions, and ones with a linear transition state at that. The role of rotation in reactions where the H atom is transferred between bulkier species is at present under investigation, as is the role played by the geometry of the transition state. Another caveat is that these calculations are valid only if classical mechanics gives an adequate description of the dynamics of the particles. This is the subject of current investigation. However, we believe that our data were obtained at such high total energy that the trajectory approach should predict at least the qualitative trends.

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Formation of Very Large Gold Superclusters (Clusters of Clusters) as Secondary Ions up to $(Au_{13})_{55}$ by Secondary Ion Mass Spectrometry

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Secondary ion mass spectrometry (SIMS) and plasma desorption mass spectrometry (PDMS) have been used in a systematic study to characterize different metal complexes. Both desorption techniques in combination with a time-of-flight (TOF) analyzer allow the investigation of molecular weight, fragmentation pathways, and metastability of secondary ions. Especially for ligand-stabilized metal clusters, mass spectrometry gives important information about the structure of these compounds. By means of SIMS and PDMS spectra the structure principle of the $Au_{55}(PPh_3)_{12}Cl_6$ complex is clarified to be cubic (ccp) or hexagonal (hcp) close packing.

There is an open question concerning the structure of high-nuclearity metal clusters. Two main structure types are in discussion: (1) vertex-sharing icosahedra, building upon each unit to form highly symmetric supraclusters;[1,2] and (2) cubic close packed (ccp) or hexagonal close packed (hcp) with the outer geometry of a cuboctahedron.[3] It is well-known that for smaller clusters both structures have been observed. From a theoretical point of view, the density of an icosahedral packing of atoms of the same size is lower than the density of ccp or hcp structures. Therefore it is assumed that for higher nuclear clusters icosahedral packings must sometimes collapse into the dense packed state. Up to now clusters of higher nuclearity have never been observed with an icosahedral structure.

Recently Fackler et al.[4,5] referred some peaks in the SI spectra of $Au_{55}(PPh_3)_{12}Cl_6$ to the icosahedral packing of this gold complex.[6] In this study, mass spectra were recorded with PDMS whereby broad mass distributions in the higher mass range (m < 50 000 u) were found. The most abundant SI peaks at 8200 u, 12 800 u and 16 600 u are explained by the fragmentation of vertex-sharing supraclusters as described by Teo et al.[2] The final conclusion of this work is that Schmid's formula of this gold complex has to be corrected to $Au_{67}(PPh_3)_{14}Cl_8$.

In our experiments, measurements were carried out with a new PDMS/SIMS combination TOF mass spectrometer. This instrument can be used for comparative studies of secondary ion formation on identical samples under keV- and MeV-ion impact.[7] The instrument is described in detail elsewhere.[8,9]

The samples were dissolved in CH_2Cl_2 and dropped onto aluminum or silver foil. Negative as well as positive PDMS and SIMS spectra were taken from different sample thicknesses.[10]

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Table I. Measured and Calculated Values[a] for the Peak Centers of $(Au_{13})_n^+$ in the Positive SIMS Spectra of the Gold Complex Sample

first series			second series			third series		
measd	calcd	*n*	measd	calcd	*n*	measd	calcd	*n*
7700	7682	3	12 800	12 803	5	17 900	17 924	7
18 000	17 924	7	22 500	23 045	9	38 400	38 408	15
33 300	33 287	13	43 500	43 530	17	58 900	58 893	23
			84 500	84 499	33	79 400	79 378	31
						99 500	99 862	39
						119 000	120 347	47
						139 000	140 831	55

[a] In unified atomic mass units.

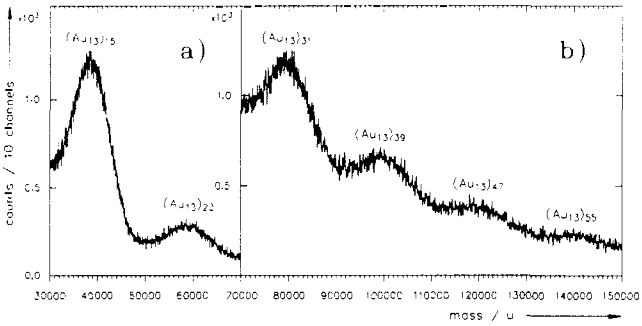

Figure 1. Positive SIMS spectrum of the investigated gold complex: sample thickness = 10^{-7} mol/cm^2; (a) primary ion dose density (PIDD) = 2.9×10^{11}/cm^2; (b) PIDD = 2.6×10^{12}/cm^2.

A detailed description of the results will be given in a subsequent report.[11] This work is focused on the high mass range of the SI spectra, where both desorption techniques give broad mass distributions.[12] Three series of SI peaks are found in the positive spectra whereby the masses of the largest SI obtained in these series increase with the layer thickness. Table I gives a comparison of the measured peak centers in the positive SIMS spectra with the calculated values for multiples of $(Au_{13})_n^+$. Only the first of these three series appears in the PDMS spectra. Starting with mass m = 38 400 u (n = 15), the third peak series is shown in Figure 1 up to mass m = 140 000 u (n = 55). In the negative spectra, a peak centered at 15 400 u ($(Au_{13})_6$) is measured with SIMS and PDMS (thin sample); a second peak at 20 500 u ($(Au_{13})_8$) appears only in the SIMS spectra (thick sample).

All SI peaks in the higher mass range can be explained very well by $(Au_{13})_n^{+/-}$. The main consequences of our results are the following.

1. *The metal complex $Au_{55}(PPh_3)_{12}Cl_6$ has a hcp or ccp structure.* Magic numbers for sphere packings are an expression of shell-closing effects. Depending on the real structure, these numbers must appear in the mass spectra.[13] Magic numbers of a two-shell cluster (hcp or ccp metal) are 13 and 55. Clusters containing u × 13 gold atoms dominate the SI spectra of the investigated gold complex, so that the assumption of a dense packed structure seems to be correct. In our opinion the formed SI are "clusters of clusters", where the thermodynamically stable Au_{13} particle behaves like a new "big atom". These new atoms again try to form "close-packed" structures. These results agree completely with those obtained on a preparative scale. $Au_{55}(PPh_3)_{12}Cl_6$ as well as a series of other M_{55} clusters can be degraded in solution to naked M_{13} particles which serve as building blocks for microcrystalline $(M_{13})_n$ super clusters.[3] As these novel modifications were found to consist of ccp M_{13} clusters, one can conclude that the Au_{13} particles generated by SIMS possess the same structural features. Consequently this must also be valid for the M_{55} clusters, so that Fackler's proposal[4] must be rejected.

2. *SIMS is well-suited for the investigation of metal complexes.* The desorption process and especially the yield of SI in SIMS and PDMS are mainly determined by the energy loss of the primary particles (stopping power). As primary particles in the MeV range interact mainly with target electrons (electronic stopping power), the SI yield is much higher from a dielectric than from a metallic surface. The opposite holds for SIMS, where the energy loss is due to elastic and inelastic collisions between primary particles and target atoms (nuclear stopping power). As the metallic character of metal complexes and especially of metal clusters is more pronounced,[14] SIMS is superior to PDMS in characterizing these substances.

3. *The formation of large SI in the mass range about 100 000 u with SIMS is possible.* Formation of large SI masses is well-known for MeV-ion bombardment; multiply charged cluster ions of peptides with SI masses up to 50 000 u have been observed.[15] On the other hand, SI formation in SIMS for most substance classes has been reported only for SI masses below 15 000 u (static SIMS), with the exception of metal clusters (26 000 u (dynamic SIMS)[16]). Therefore this is the first report about the formation of SI with masses above 100 000 u by primary ion impact.

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(10) The same amounts of solutions with different concentrations (10^{-4}–10^{-2} mol) were deposited onto the targets. The sample thickness varied between 10^{-9} mol/cm^2 and 10^{-7} mol/cm^2.

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(12) The widths of these distributions are similar to that measured by Fackler et al. A possible explanation may be that the large number of atoms involved in this cluster formation process leads to a statistical error by the formation of the SI (more or less metal atoms, additional ligands). Also the different peaks are mixed by the isotopic pattern due to the additional ligands (C, Cl, H) and broadened by the energy distribution of the SI. These peaks cannot be resolved, because in this mass range one channel of the registration system contains up to 10 Da (daltons).

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Time-Resolved Photodissociation of Methylnaphthalene Ion. An Illustration of Kinetic Shifts in Large-Ion Dissociations

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A long-standing puzzle of ion thermochemistry is why the cleavage of a methyl hydrogen from the methylnaphthalene ion appears to require perhaps 2 eV more energy than the cleavage of a similar methyl hydrogen from the apparently analogous toluene ion.[1] Time-resolved photodissociation measurements described here show that this apparent discrepancy is an artifact of the large kinetic shift in the dissociation, and that the dissociation thermochemistry of these two systems is actually quite similar, with activation energies estimated in the vicinity of 2 eV in both cases. Resolution of this problem is of interest particularly because the stability of $C_{11}H_9^+$ ions plays a role in the literature of aromatic stability.[2]

The surprisingly high threshold (around 4 eV) previously assigned to methylnaphthalene ion dissociation derives from a

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