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.

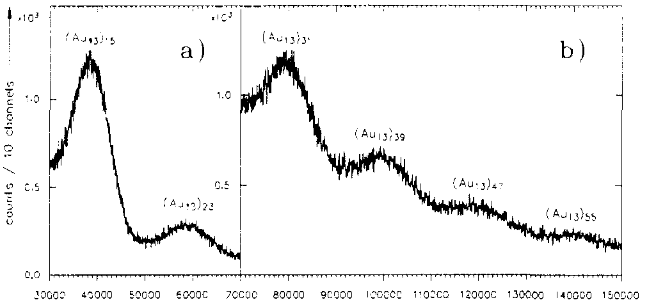

Figure 1. Positive SIMS spectrum of the investigated gold complex: sample thickness = 10^{-7} mol/cm^2; (a) primary ion dose density (PIDD) = 2.9×10^{11}/cm^2; (b) PIDD = 2.6×10^{12}/cm^2.

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.

(11) Feld, H.; Leute, A.; Rading, D.; Benninghoven, A.; Schmid, G., *Z. Phys.* D. In press.

(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).

(13) Echt, O.; Sattler, K.; Recknagel, E. *Phys. Rev. Lett.* **1981**, *47*(16), 1121.

(14) A dried solution of the gold metal complex is a system consisting of very small metal particles in a dielectricum with the physical behavior of a semiconductor (see ref 3).

(15) Sundqvist, B. U. R.; Ariyaratne, A.; Ens, W.; Fenyö, D.; Hedin, A.; Hakansson, P.; Jonsson, G.; Widdiyasekera, S. In *Ion Formation from Organic Solids (IFOS IV)*; Benninghoven, A., Ed.; John Wiley & Sons: New York, 1989.

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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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(1) Honovich, J. P.; Segall, J.; Dunbar, R. C. *J. Phys. Chem.* **1985**, *89*, 3617.

(2) For example: Glidewell, C.; Lloyd, D. *Tetrahedron* **1984**, *40*, 4455. Ilic, P.; Trinajstic, N. *J. Org. Chem.* **1980**, *45*, 1738.

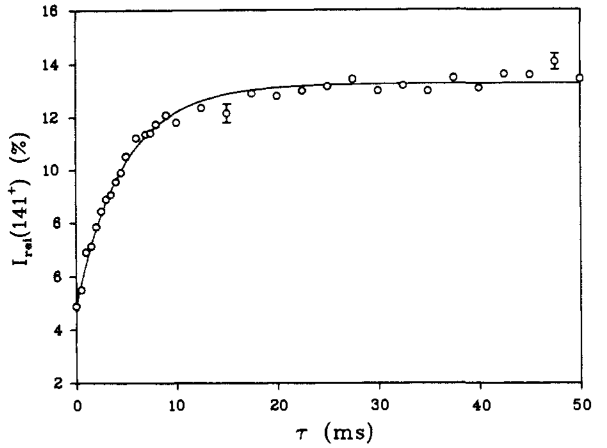

Figure 1. Time profile of $C_{11}H_9^+$ product ion appearance following the 355-nm laser pulse. The solid curve is the predicted profile using the RRKM rate–energy function (Figure 2) convoluted with a thermal parent ion distribution at 350 K.

consensus of several gas-phase appearance-energy measurements.[1,3-5] One thermochemical value,[6] near 3 eV, is somewhat closer to the cleavage activation energy for methylnaphthalene ion anticipated by analogy with toluene ion (whose activation energy was recently reported as 1.7 eV[7]).

The unreasonable magnitude and the general uncertainty surrounding the methylnaphthalene ion data set typify the unsatisfactory status of the thermochemistry of many large ionic molecules. The present paper shows, by solving the methylnaphthalene ion problem, that such doubts are well founded, but that valid thermochemistry is derivable from time- and energy-resolved dissociation studies. A very large kinetic shift, of the order of 2 eV in this case, frustrates measurements based on fragmentation appearance energies. However, measurements of the dissociation rate by time-resolved photodissociation, at internal energies as close to threshold as is feasible, can be extrapolated with confidence to a true activation energy of 2.25 ± 0.2 eV.

The dissociation of 1-methylnaphthalene ion (eq 1) was observed at 355 and 308 nm by time-resolved photodissociation in the ion cyclotron resonance (ICR) ion trap.[8] In this technique the

$$C_{11}H_{10}^+ \rightarrow C_{11}H_9^+ + H \qquad (1)$$

population of parent ions (generated by electron impact) is thermalized by collisional and radiative relaxation (1.3 s at a pressure of 1×10^{-6} Torr). Dissociation is initiated by a 10-ns laser pulse, and the appearance of dissociation product ions is time resolved on a time scale ranging from a few microseconds to many milliseconds. An illustrative time-resolved spectrum for 1-methylnaphthalene ion is shown in Figure 1. The time constants for product ion formation were observed to be 5.0 ms at 355 nm and 1.5 ms at 308 nm.

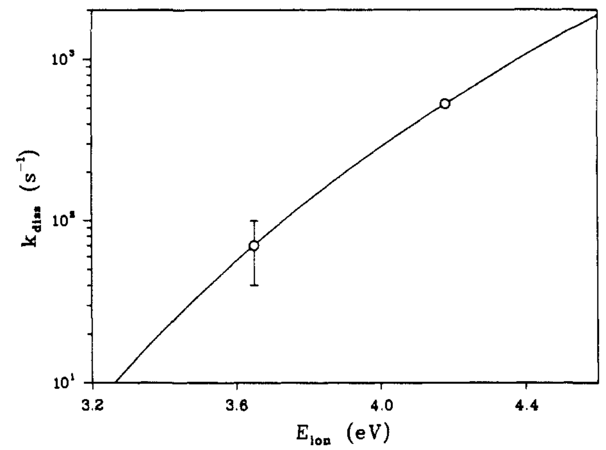

Figure 2. The dissociation rate points derived from the photodissociation results at 355 and 308 nm, along with the RRKM rate–energy curve best fitting the points.

Table I. Kinetic Shifts for $C_{11}H_9^+$ Appearance Calculated from the Rate–Energy Curve Shown in Figure 2

type of kinetic shift	kinetic shift, eV	threshold,[b] eV
conventional	2.15	4.4
intrinsic	1.05	3.3
true value	0	2.25

[a] Excess of the observed appearance threshold over the true activation energy for the dissociation process. [b] The excitation energy needed in the parent $C_{11}H_{10}^+$ to give observed production of fragment ions according to the criteria described in the text.

Accurate determination of rate–energy values from the time-resolved dissociation curves requires deconvolution of the effect of the thermal spread of internal energies,[8] and also consideration of the effects of radiative and collisional relaxation of the photoexcited ions (which can be severe for such slow dissociations). After allowance was made for the known radiative relaxation rate (~130 s^{-1}) of the parent ion,[9] rates of dissociation were assigned as 70 ± 30 s^{-1} at 355 nm (3.6 eV internal energy) and 530 ± 30 s^{-1} at 308 nm (4.2 eV energy).

These two dissociation rate constants establish both the magnitude and the slope of the dissocition rate–energy curve, as shown in Figure 2. The most useful way to interpret these results is by modeling using RRKM theory.[10,11] The low slope of the experimental curve requires the assignment of a tight transition state to the process. The RRKM curve best fitting the observed points (shown in Figure 2) has[11-13] an E_0 of 2.25 ± 0.2 eV and a ΔS_{1000K} of −15 ± 5 cal K^{-1}.

Both toluene ion[7] and methylnaphthalene ion exhibit tight transition states for loss of hydrogen at low internal excitation. For toluene ion, this has been attributed to rearrangement to the tropylium product ion structure. If the observed tight transition state for methylnaphthalene ion corresponds to rearrangement to a benzotropylium ion structure, then the observed activation energy of 2.25 eV for dissociation is actually an activation energy for ion rearrangement, and only sets an upper limit on the thermochemical endothermicity of dissociation to this product ion structure.

The large number of degrees of freedom and the tight transition state lead to massive kinetic shifts for reaction 1. Table I lists

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(8) Dunbar, R. C. *J. Phys. Chem.* **1987**, *91*, 2801; *J. Chem. Phys.* **1989**, *91*, 6080.

(9) Derived from measurements reported by Ahmed (Ahmed, M. S. Ph.D. Thesis, Case Western Reserve University, 1988). The fact that more than 20% of the photoexcited ions were observed to dissociate before relaxation sets a lower limit of 40 s^{-1} on the dissociation rate constant at 355 nm.

(10) As was done, for instance, in the following: Dunbar, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 5572.

(11) For a discussion of the significance of these RRKM parameters with regard to the tightness or looseness of the transition state, see: Lifshitz, C. *Adv. Mass Spectrom.* **1989**, *11*, 713.

(12) The present technique was unfortunately not able to extend the range of useful rate–energy points in this system. At longer wavelength, the dissociation would be overwhelmed by radiative relaxation of the photoexcited ion, while at a wavelength shorter than 308 nm (266 nm was tried), multiphoton ionization of residual neutral methylnaphthalene in the cell made it impossible to observe the photodissociation process.

(13) The error limits are largely determined by the range of acceptable RRKM fits passing through the rather uncertain 355-nm point. Note that the wide error limits on the 355-nm point are not experimental, but result from the uncertainty in the appropriate correction for radiative relaxation. The ΔS value of −15 eu is unusually large in (negative) value, and a less negative number might be preferred. A value of −8 eu is the least negative value giving a fit to the two data points within their error limits; this corresponds to an E_0 value of 2.42 eV, leading to our estimate of an upper limit of about 2.45 eV for E_0.

calculated kinetic shifts for two measurement approaches. The "conventional" kinetic shift is taken as the energy above E_0 needed to give 1% fragmentation within 10^{-5} s, appropriate to conventional mass spectrometer appearance measurements. The "intrinsic" kinetic shift is taken as the energy needed for 10% fragmentation in competition with radiative relaxation of the excited ion, appropriate to an ion-trap appearance-energy experiment unlimited by ion containment time.

These large kinetic shifts account for the high thresholds obtained even in previous ion-trap work.[1] In the presence of major kinetic shifts, only determination of two or more points on the rate–energy curve (for instance, by photodissociation, PEPICO,[15] or MPI[16]), accompanied by RRKM modeling, leads to useful information about the dissociation activation energy.[14] In the methylnaphthalene case, this leads to a new upper limit on the heat of formation for $C_{11}H_9^+$ of ≤869 ± 20 kJ mol^{-1} (most likely referring to the benzotropylium structure).[17]

Acknowledgment. Support of this work from the National Science Foundation and from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(14) Only the technique of radical ionization[6] avoids entirely the uncertainty introduced by kinetic shifts, and it may have given a valid measurement of the heat of formation of the methylnaphthylium ion (but no information about the benzotropylium ion).

(15) For instance: Baer, T; Dutuit, O.; Mestdagh, H.; Rolando, C. *J. Phys. Chem.* **1988**, *92*, 5674.

(16) For instance: Neusser, H. J. *J. Phys. Chem.* **1989**, *93*, 3897.

(17) As expected, this is much lower than the previous value of 962 kJ/mol given in the following: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, *Suppl. 1*.

Synthetic $NiFe_3Q_4$ Cubane-Type Clusters ($S = {}^3/_2$) by Reductive Rearrangement of Linear $[Fe_3Q_4(SEt)_4]^{3-}$ (Q = S, Se)

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Heterometal cubane-type clusters MFe_3S_4 containing biological metals such as Co, Ni, and Zn cannot be prepared by assembly reactions analogous to those producing M = V,[1] Mo,[2] W,[2] and Re[3] clusters, owing to the absence of appropriate thiometalate precursors $[MS_4]^{z-}$. However, incubation of proteins having cuboidal Fe_3S_4 clusters with M^{2+} salts affords protein-bound species, which, while structurally undefined, possess electronic properties indicative of the integration of M = Co,[4] Ni,[5] Zn,[6,7] or Cd[7] and Fe_3S_4 into a common, presumably cubane-type, unit. Noting that the linear $[Fe_3S_4(SEt)_4]^{3-}$ (**1**) → cubane $[Fe_4S_4(SEt)_4]^{2-}$ cluster conversion in the system **1**/$FeCl_2$/NaSEt[8] proceeds by an effective two-electron reduction of **1**, we investigated reaction 1 (Q = S, Se) with two trinuclear precursors which differ appreciably in their reducibilities [E_{pc}(**1**) = −1.66, −1.79 V (MeCN); E_{pc}(**2**) = −1.18, −1.24 V (DMF)].[9] Previously unreported $[Fe_3Se_4(SEt)_4]^{3-}$ (**2**) was prepared analogously to **1**[8] (67%) and derivatized (4 equiv of PhSH) to $[Fe_3Se_4(SPh)_4]^{3-}$ (**3**, 68%), which was proven by crystallography to have the linear trinuclear structure (Fe–Fe–Fe, 180°; Fe–Se, 2.321 (1)–2.365 (1) Å; Fe–Fe, 2.781 (1) Å.[10]

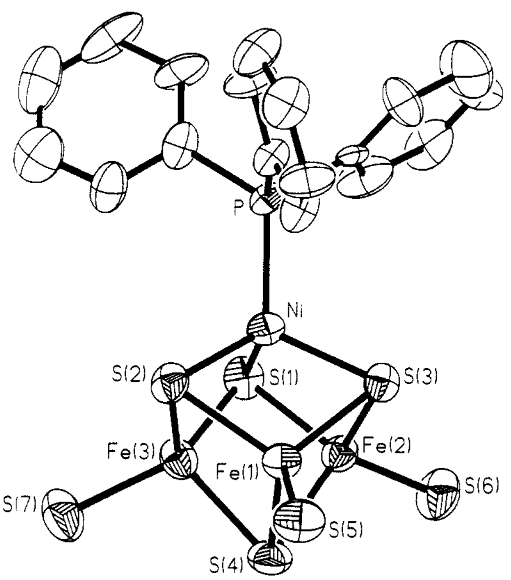
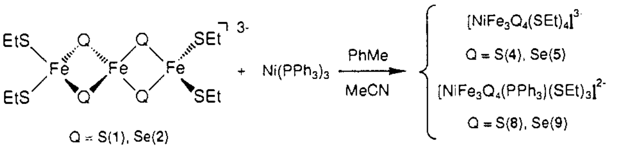


Figure 1. Structure of cluster **8** as its Et_4N^+ salt, showing 30% thermal ellipsoids and the atom-labeling scheme. Mean values of the indicated distance (Å) or angle *type* under idealized C_3 symmetry: Ni–Fe, 2.69 (2); Ni–S, 2.262 (6); Fe(3)–S(2), 2.306 (8); Fe(2)–S(4), 2.297 (8); Fe(3)–S(1), 2.269 (7); Fe(1)–S(5), 2.283 (6); P–Ni–S, 113 (2)°; S–Ni–S, 105.8 (7)°. Also: Ni–P, 2.174 (6) Å; Ni···S(4), 3.824 (7) Å. Esd's of individual distances and angles are 0.004–0.008 Å and 0.1–0.3°, respectively.



(1)

The residue after solvent removal from equimolar reaction 1 (6 h) was treated in two ways.[9] (i) Thorough washing with toluene followed by recrystallization (acetonitrile/ether) gave **4** or **5** (50–60%); **4** contained a 10–15% impurity of $[Fe_4S_4(SEt)_4]^{3-}$ (**6**)[11] which could not be separated. These two clusters were identified by their isotropically shifted ^{1}H NMR spectra:[9] **4**, δ 58.5, 5.80,

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(1) Kovacs, J. A.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 702, 711.

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(9) All reactions and measurements were performed under anaerobic conditions. Clusters were isolated as Et_4N^+ salts; purified yields are given. Potentials are referenced to the SCE and isomer shifts to Fe metal at 298 K. ^{1}H NMR spectra were measured in CD_3CN; ethyl group shifts are given in the order CH_2, CH_3 (Fe, Ni). The Ni–SCH_2CH_3 signals of **4** and **5** were obscured by other resonances.

(10) X-ray structures were solved by standard procedures; empirical absorption corrections were applied. Crystallographic data are given as *a*, *b*, *c* (Å); β, space group, *Z*, unique data ($F_o^2 > 3\sigma(F_o^2)$), $R(R_w)$ (%). $(Et_4N)_3$[**3**] (173 K): 27.591 (5), 11.124 (2), 20.961 (3) Å; 118.18 (1)°, $C2/c$, 4, 3290, 4.9(5.6). $(Et_4N)_3$[**5**] (203 K): 11.596 (2), 36.768 (6), 11.848 (2) Å; 106.79 (2)°, $P2_1/n$, 4, 3541, 4.5(4.9). $(Et_4N)_3$[**7**] (173 K): 11.639 (4), 36.774 (7), 11.875 (2) Å; 106.79 (2)°, $P2_1/n$, 4, 4255, 6.2(6.3). $(Et_4N)_2$[**8**] (298 K): 13.338 (5), 14.657 (7), 26.627 (9) Å; 100.46 (3)°, $P2_1/n$, 4, 2717 (4σ), 9.5(10.3). $(Et_4N)_2$[**9**] (273 K): 13.467 (3), 14.353 (2), 27.112 (4) Å; 102.20 (1)°, $P2_1/n$, 4, 5257, 5.36(6.22). The structure of **5** was refined with a 25%/75% Ni/Fe site occupancy.

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