Binary Metal Alloy Clusters

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Binary alloy clusters $A_n B_m$ (A, B: Bi, Sb, Pb, Ag, in different compositions) have been generated by simultaneous inert gas condensation of the two vapours. Under suitable condensation conditions the adsorption of single atoms A to clusters B_m can be studied. The adsorption probabilities are found to vary with cluster size. The cluster reactivities depend on the number of absorbed foreign atoms. Lead and bismuth clusters are found to be highly reactive in cracking the strongly bound Sb_4-tetrahedron. One single interaction channel is found for Pb_n/Sb_4 (symmetrical dissociation) and three interaction channels are found for Bi_n/Sb_4 (symmetrical and nonsymmetrical dissociation). Pb- and Bi-clusters have different onset thresholds for dissociative reactivity.

PACS: 36.40; 82.65; 81.20.6

1. Introduction

Since the development of new cluster sources during the last few years several studies on reactions of molecules with clusters have been reported. Most of these measurements focus on the reactivity of transition metal clusters for example: $Fe_n + H_2$ [1–3]; $Fe_n + O_2$, H_2S, methane [4]; $Pt_n +$ benzene and several hexanes [5]; Fe_n, Co_n, Ni_n, Nb_n with H_2, D_2, N_2, or CO [6]. Binary clusters have also been produced by combining the atoms or molecules of two elements in the vapour phase: Cs vapour has been allowed to react with O_2, Cl_2, S_8, H_2O, and P_4 [7].

Metal alloy clusters Ni_n/Cr_m and Ni_n/Al_m have been studied after vapourization of the corresponding bulk alloys followed by a free jet expansion of a He/cluster mixture [8]. For clusters larger than about six atoms a statistical behaviour for the interaction between the two components is observed. For smaller clusters departure from a statistical behaviour is found, i.e. their size distributions are not correlated to the initial atomic abundances of the two components.

Different generation methods for binary metal clusters can be applied:

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(i) Langmuir or Knudsen evaporation of binary materials

(ii) clustering of binary molecules, (a) from a gas, (b) evaporated from a solid

(iii) simultaneous growth of the two separate components, (a) atom A – atom B interactions, (b) cluster A – cluster B interactions

(iv) cluster growth followed by single atom (or molecule) addition.

In this paper we mostly deal with point (iv). Binary clusters from Bi, Sb, Pb, and Ag atoms are considered [9, 10]. The clusters are generated in an inert gas condensation source with two separate ovens being applied.

The clusters are ionized (by electron bombardment) for time of flight mass analysis. Despite the charged clusters are detected we interpret the data in terms of the neutral clusters. This seems to be valid for low enough ionizing energies (soft ionization).

2. Experimental

The clusters are generated by simultaneous condensation of the two vapours in cold He gas. The source is shown in Fig. 1. The inert gas condensation method has been described earlier [11]. Two ovens with resis-
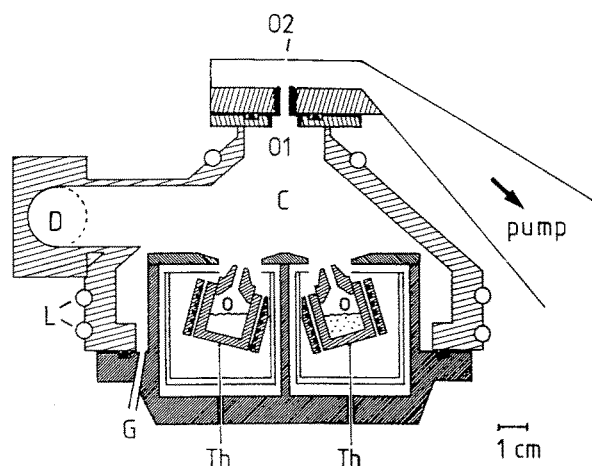
Fig. 1. Cluster source: Two metals are separately evaporated from two ovens, respectively. The ovens are resistantly heated, and the temperatures are measured with thermoelements at the bottom. Thermal shielding is provided by Ta-cylinders and Cu-walls. Condensation occurs in cold He-gas in the region C. The He-gas is cooled by the walls of the cell (G, gas inlet; D, differential pressure monitor; L, tubings for the cooling fluid). A differential pumping section is applied above the aperture 01. The clusters enter the mass spectrometer by aperture 02 [10]

tance heating are shielded by Ta-cylinders and surrounded by LN_2-cooled Cu-walls. The vapours of the two components A and B, respectively, are directed towards the condensation region of the cell there being supersaturated in cold He-gas (temperature 80 K, pressure 1 mbar). By variation of the vapour pressures relative to each other different conditions for cluster growth are obtained:

(a) $p_A \sim p_B$; clusters with a broad variety of combinations n/m are produced

(b) $p_A \gg p_B$; clusters A_n are produced, single atoms B are adsorbed at A_n.

With the conditions under (b) size dependent adsorption probabilities can be studied. If the component B is a molecular unit (for example Sb_4) dissociative reaction probabilities are gained.

After formation, the clusters leave the condensation cell. Then they are ionized by a pulsed electron beam and their masses are analysed by electronic time of flight spectrometry.

3. "Soft" Ionization

The aim of these studies is to get information about the formation of the neutral compound clusters. For mass spectrometry, however, the clusters have to be ionized. At electron ionizing energies close enough to the ionization threshold we suppose that the ion-

ized-cluster spectrum reflects the neutral-cluster spectrum.

This becomes obvious if cluster spectra are compared being taken with different ionizing energies. Antimony is an interesting model substance because the vapour itself already contains cluster units. These are highly stable Sb_4-clusters with all valence bonds saturated in a tetrahedron structure (bond energy ~ 3 eV). A modulo 4 sequence is expected in the mass spectrum if no intramolecular fragmentation occurs.

In common we have to consider two size distributions: (i) the distribution of the neutrals, and (ii) the distribution of the cluster ions. In the mass spectrum we analyse the ions alone and one would think that the spectrum reflects their stability distribution. In the case of Sb-clusters, however, this expectation does not hold at all. The high tendency for covalent bond formation with this material is expected to lead to geometrical structures for the cluster ions being completely different from that of the neutrals. Both, the neutral and the charged clusters should have their characteristic stability distributions (high tendency for chemical inertness for all cluster sizes) and the two distributions are expected to be fundamentally different. Despite the charged clusters are detected we will show in the following section that in the case of Sb-clusters the stability distribution of the charged clusters does not show up.

Figure 2a shows a mass spectrum of antimony clusters with a sequence of Sb_{4n}-peaks alone. For a discussion we first compare the neutral and the charged Sb_4-cluster: The Sb-atom in the Sb_4-complex provides 3 $5p$-electrons for chemical bonds. The six bonds in the tetrahedron structure are fully saturated by paired electrons the Sb_4 therefore being a highly stable inert unit. The total number of valence electrons is 12 and thus the high stability is explained by the "even electron rule". The ionized cluster Sb_4^+ contains 11 valence electrons and does not fulfill the even electron rule while Sb_3^+ (8 valence electrons) does. From Fig. 2a however we see that Sb_3^+ is not detected in the mass spectrum. This result is found for low electron energies $E_i < 10$ eV. For E_i just above the ionization threshold the energy transferred to the cluster is not high enough for fragmentation processes to occur.

We conclude that ionization alone does not necessarily lead to fragmentation even if the charged clusters have a size distribution different from that of the neutral clusters. This is illustrated in the case of Sb_{4n}-cluster-spectra. The ionized clusters Sb_{4n}^+ do not fulfill the "even electron rule". A stability distribution of the singly charged Sb_{4n}-clusters would show preference for clusters with odd numbers of atoms. At low electron ionizing energy the stability distribution of
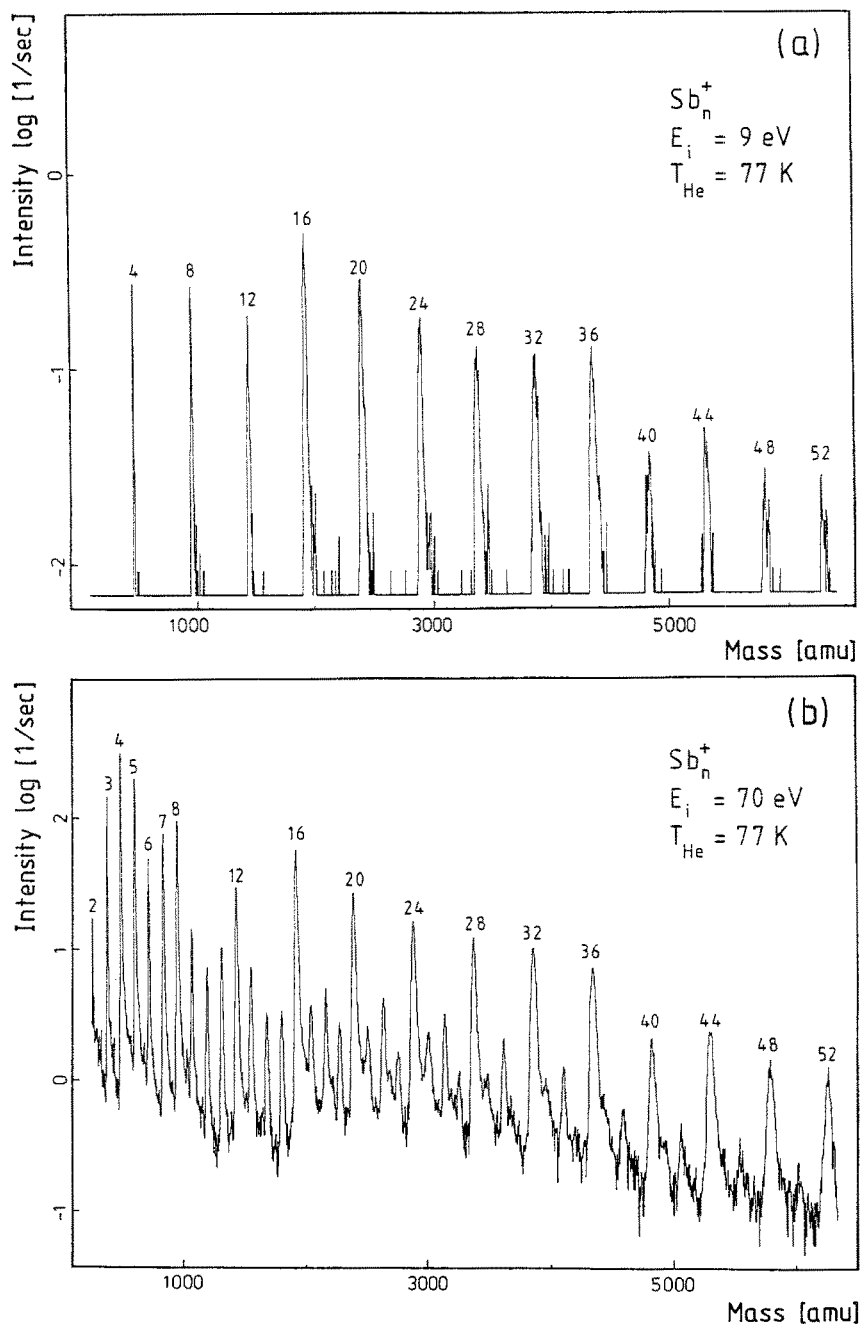
Fig. 2a and b. Mass spectra of Sb-clusters for two different electron ionizing energies E_i: **a** $E_i=9$ eV, **b** $E_i=70$ eV. The temperature of the He-gas in the source is $T_{He}=77$ K [10]

the neutral clusters however cannot be transferred into the stability distribution of the charged clusters because there is a redistribution barrier for this process to happen. Only if E_i is increased above the various appearance potentials for fragmentation, highly stable ionized clusters are observed (for example, Sb_3^+, Sb_5^+, see Fig. 2b).

Fragmentation after electron impact has been studied in detail for the antimony tetramer [12]. The ionization potential (IP) of Sb_4 is 7.7 eV and the lowest appearance potential $AP=10.4$ eV is found for

the reaction $Sb_4+e^- \rightarrow Sb_3^+ +Sb+2e^-$. This shows that at least $(AP-IP)=2.7$ eV has to be transferred to a Sb_4-molecule to fragment. This is about the same as the bond dissociation energy of the neutral Sb_4-molecule $D(Sb_3-Sb)=2.9$ eV.

The bond dissociation energies of small charged Sb cluster ions are high as well $(D(Sb_3^+-Sb)=2.7$ eV, $D(Sb_2^+-Sb_2)=3.8$ eV, $D(Sb^+-Sb)=3.2$ eV [12]), being derived from ionization potential measurements of Sb_3 $(IP=7.5$ eV) and Sb_2 $(IP=8.6$ eV). These species are present in the vapour at high enough temper-

ature of the Knudsen cell. For the studies reported here Sb-vapour has been produced at temperatures low enough to consist predominantly of Sb_4-molecules.

A recent study on Bi-clusters showed similar results: onset for fragmentation in the vicinity of 10.5 eV [13]. This is 3.2 eV above the ionization potential of Bi_1 (7.7 eV). The bond dissociation energies for dimers of Bi, Sb, Pb, and Ag atoms lie between 0.8 eV and 3.1 eV: $Bi-Bi$, 2.1 eV; $Sb-Sb$, 3.1 eV; $Pb-Pb$, 0.8 eV; $Ag-Ag$, 1.7 eV; $Bi-Ag$, 2.0 eV; $Bi-Sb$, 2.6 eV; $Bi-Pb$, 1.5 eV (taken from phys. Tables). Therefore AB-bonds could be expected to have similar strength in the clusters as AA or BB bonds. This however does not hold anymore if "chemically inert" subunits can build up in the cluster. Then a situation is created where the same kind of atoms is bound under different conditions and with strongly differing bond strengths.

So far we did not discuss intermolecular fragmentation $Sb_{4n}^{+\ *} \rightarrow Sb_{4(n-1)}^{+} + Sb_4$. This would be important if the inert Sb_4-units would be packed in Sb_{4n} with loose intermolecular Van der Waals bond. From the data now in hand concerning their reactivity, however, we doubt if the Sb_4 units retain their identity after being clustered.

For interpretation of the data a further point has to be considered. For ionizing energies E_i close enough to the ionization potentials IP of the clusters one expects that the cross section for ion formation depends on the difference $(IP-E_i)$ which is a function of n for $IP(n)$. This would lead to the detection of different cluster intensities for different n being generated during ionization. In this case the measured mass distribution would neither reflect the equilibrium intensities of the neutral nor that of the ionized clusters. In order to check this possibility we varied E_i but the main features in the spectra being concerned with these studies did not change.

4. Adsorption of Single Atoms

We now consider the adsorption of single Ag-atoms on Sb_{4n}-clusters. Figure 3 shows a mass spectrum of Sb/Ag-clusters and the corresponding histogram for the integrated intensities. Two features can be seen: (i) up to three Ag-atoms are adsorbed and (ii) for most cluster sizes the intensity $I(Sb_{4n}Ag_m)$, $m=1-3$, decreases fast with increasing m. Physisorption seams to be relevant for these cases. However, Fig. 3 shows two exceptions, Sb_8 and Sb_{12}: For these clusters the probability for one Ag-atom to be adsorbed is especially high.

The adsorption probability can be defined as follows:

$$P_a(n) = I(Sb_nAg_m^+)/\{I(Sb_n^+) + \sum_m I(Sb_nAg_m^+)\};$$

$$m = 1-3$$

In Fig. 4, P_a is plotted as a function of n for $m=1$, 2, 3. The curve for one Ag atom adsorption shows pronounced structure, the $(m=2)$- and $(m=3)$-curves are relatively flat. For $m=1$, maxima are found for $n=8$, 12, 24, and 32. Sb-clusters with these sizes are more reactive than others in that size region.

It is difficult to understand why the adsorption of the second and third adatom at the cluster surface should be so much different from the adsorption of the first adatom. It could be explained in two ways: (i) saturation of the dangling cluster bonds by the first adatom. The clusters Sb_nAg_1 then would be inert for other adatoms, i.e. chemisorption for $m=1$, and physisorption for $m=2$ and 3; (ii) The clusters have nutshell structures with empty inner cavities and one Ag atom is situated inside the cavity. The structure in the reactivity curve then would be caused by the ability of some clusters to let an adatom move to the center or, to rearrange and incorporate the foreign atom. In this case the outstanding high intensities of Sb_8Ag_1 and $Sb_{12}Ag_1$ could be understood in terms of bcc (8 nearest neighbors) and fcc (12 nearest neighbors) structures, respectively.

For both explanations discussed above, however, geometrical structures for Sb-clusters have to be assumed which are fundamentally different from the structures assumed so far. The expectation so far was that clustering of tightly bound units like Sb_4 leads to packing of these units. They contain their individuality in the cluster. A packing model for tetrahedra explained the observed magic numbers in the Sb_{4n} mass spectra [14]. If the chemically inert Sb_4-units are packed to clusters, the ensemble should be inert as well. No variation in the adsorption probability for foreign atoms is expected in this case. The experimental data, which show strong cluster size dependence for P_a, however, seem to indicate that collective structures build up. The Sb_4-units loose their idendity after being packed and new energetically favoured atomic arrangements are generated. There is no direct proof for this statement but it could explain the pronounced structure in the $P_a(n, m)$-plots.

We cannot completely rule out the possibility that the difference between $m=1$, 2, and 3 is generated after ionization but this is not likely to occur. For a discussion of this point we first ask which one of the two components (Ag or Sb_{4n}) is ionized: In the case of Van der Waals coupling between Sb_4-units the IP's of both components $(IP(Ag)=7.57$ eV, IP $(Sb_4)=7.64$ eV, $IP(Sb_{4n}) \sim IP(Sb_4)$ for small n) are nearly the same. In the case of collective Sb_n-structures $IP(n)$ would decrease. For both
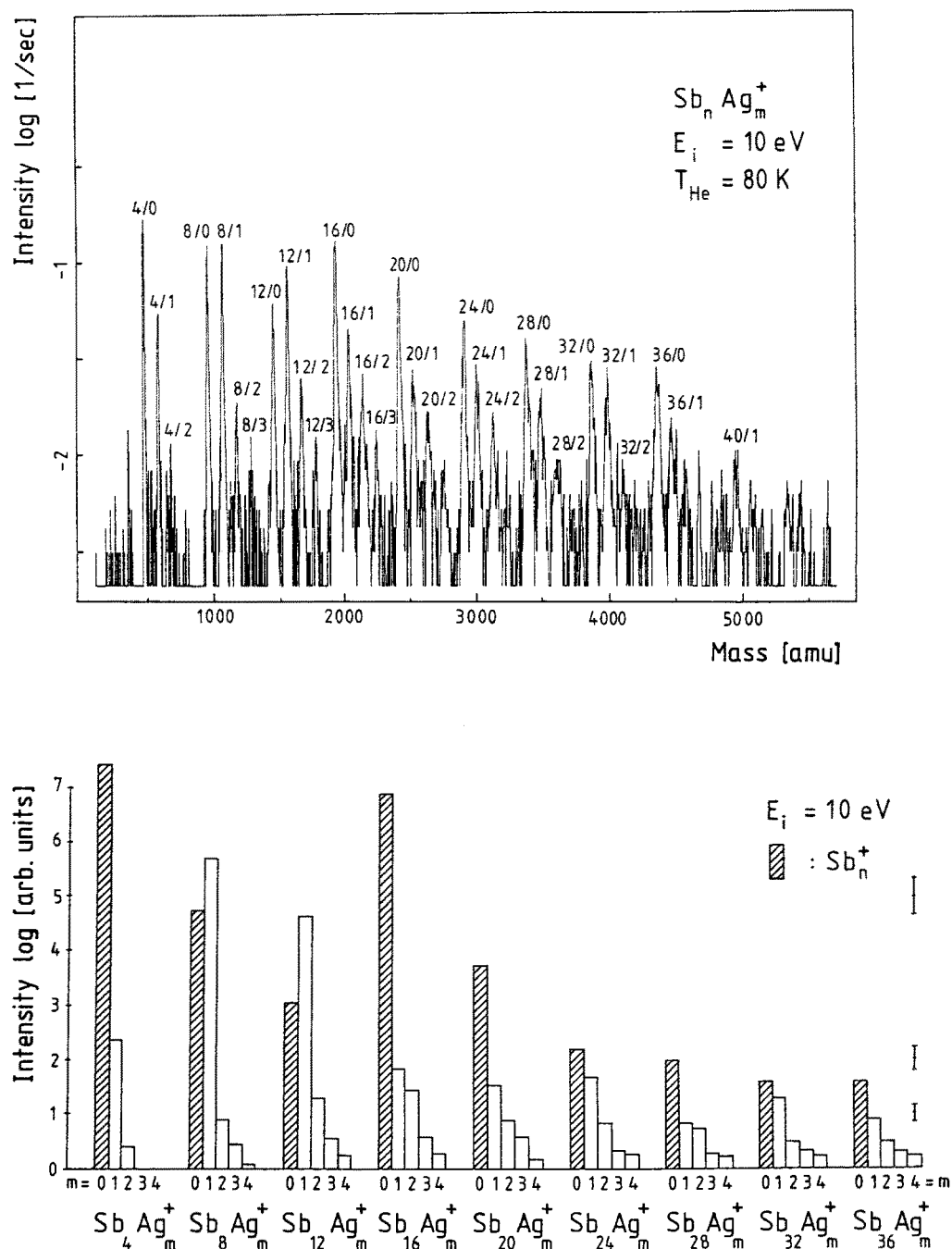
Fig. 3. Mass spectrum of Sb_nAg_m-clusters (top) and the corresponding histogram with integrated intensities (bottom); $E_i = 10$ eV [10]

Sb_n-structures the electron is not removed from the silver atom and therefore solvation of Ag^+ can be ruled out. The other possibility namely redistribution of the whole alloy cluster ion is unlikely because of the relatively high redistribution barriers of a few electron volts. As mentioned before stable cluster ions are only found predominantly for high electron ionizing energies $(E_i \gg 10$ eV) which in the case of alloy clusters will be discussed in another publication [10].

Figure 5 shows the P_a-plot for adsorption of Pb-atoms on Sb-clusters. A strong size dependence is found for $m = 1$ and 2. There is a maximum at $n = 12$, but the absolute P_a-values for $n = 8$ and 12 are much lower than in the case of Ag-adsorption. A silver atom fits into the center of an antimony cluster because the metallic radii r_0 of $Sb(r_0 = 1.39$ Å) and $Ag(r_0 = 1.34$ Å) are nearly the same. Lead atoms are much larger in size $Pb(r_0 = 1.5$ Å). Therefore, a center
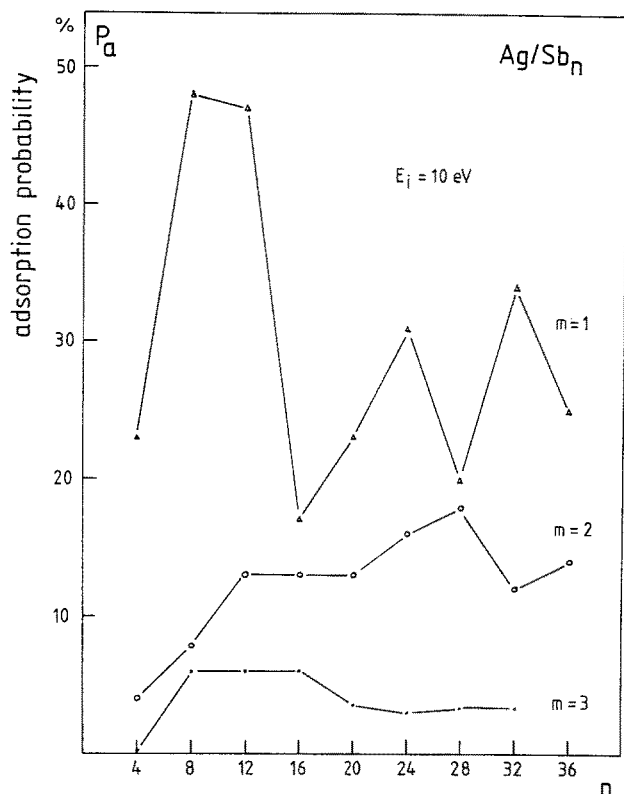
Fig. 4. Adsorption probabilities for one, two, or three Ag-adatoms on Sb-clusters (definition in the text) [10]
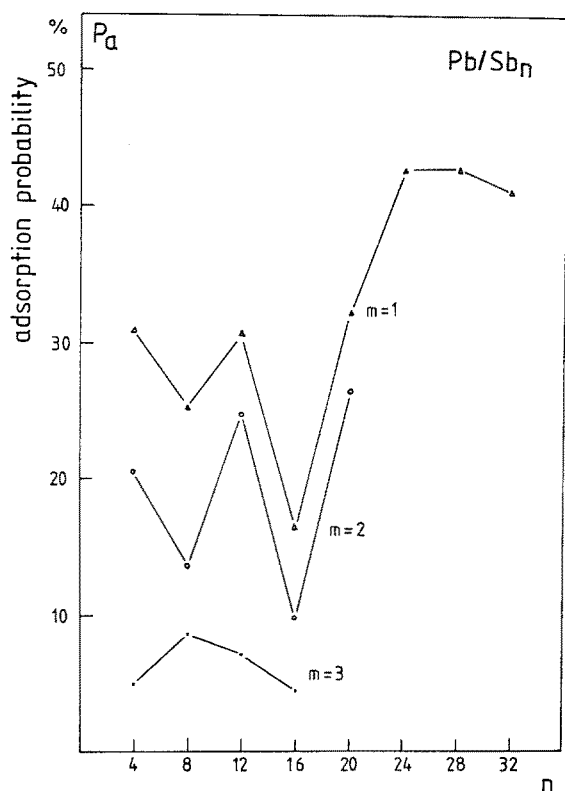

Fig. 5. Adsorption probabilities for one, two, or three Pb-adatoms on Sb-clusters [10]

position seems to be convenient for a Ag-atom but unconvenient for a Pb-atom.

5. Dissociative Chemisorption

With source conditions where Sb_4-units are adsorbed by Pb-clusters the spectrum in Fig. 6 is measured. The adsorption probabilities are extremely high. The histogram shows that one or two lead atoms do not influence the Sb_4-units. However, from Pb_3 on, very effective dissociation of Sb_4 occurs; the molecule is split into two halfs: $Pb_n + Sb_4 \rightarrow Pb_n Sb_2 + Sb_2$. Figure 7 shows the dissociation probabilities

$$P_d(n) = I(Pb_n Sb_2^+)/\{I(Pb_n Sb_2^+) + I(Pb_n Sb_4^+)\}.$$

The corresponding mass spectra have been taken at three different electron ionizing energies. The plot at 8 eV shows the dissociation onset at $n = 3$. Then, P_d increases fast with n and gets $\sim 90\%$ for $n = 10$. Three local maxima ($n = 4, 8, 10$) are found. The outstanding high reactivity can also be seen from spectra taken at 10 eV and 80 eV.

It is interesting to note that the adsorption probabilities for Sb_4 on Pb_n-clusters are extremely high (see Fig. 6). The corresponding $Pb - Sb$ bulk phase diagram is simply eutectic. We conclude that two materials which are insoluble in the bulk phase can be soluble in clusters. It is open to question if this is due to the rapid quenching of the two vapours possibly yielding metastable complexes (with life times of at least a few microseconds, the time for mass analysis), to the nonperiodic character of the cluster geometries or to the quantized electronic structure of the two components.

If one or two Sb_4-units are adsorbed by Bi-clusters the histogram in Fig. 8 is obtained. Like Pb_n, Bi-clusters are also reactive in respect to dissociation of Sb_4. In this case however, symmetric and antisymmetric dissociation channels are populated. Bi-clusters have no size threshold for the reaction onset. The single Bi-atom already affects dissociation of Sb_4.

The ability of Pb- and Bi-clusters to crack the covalent Sb-bonds is surprising. The dissociation energies are high for both dissociation paths: $Sb_3 - Sb$, 2.9 eV; $Sb_2 - Sb_2$, 2.9 eV [12]. One possible explanation is that electronic charge is transferred from the clusters into the antibonding states of Sb_4. For the single atoms we would not expect that this occurs: the electronegativities of the atoms Sb(1.9), Pb(1.8) and Bi(1.9) are nearly the same, and the ionization potentials as well (Sb_4, 7.7 eV; Pb_1, 7.42 eV; Bi_1, 7.29 eV). IP's for clusters however decrease fast with increasing size ($\sim n^{-1/3}$ for metals and $\sim n^{-1}$ for insulators) towards the bulk work functions (4.04 eV for
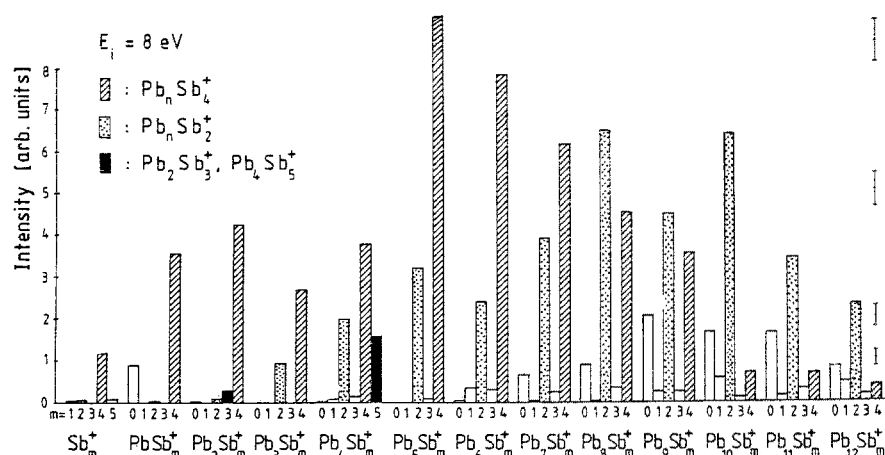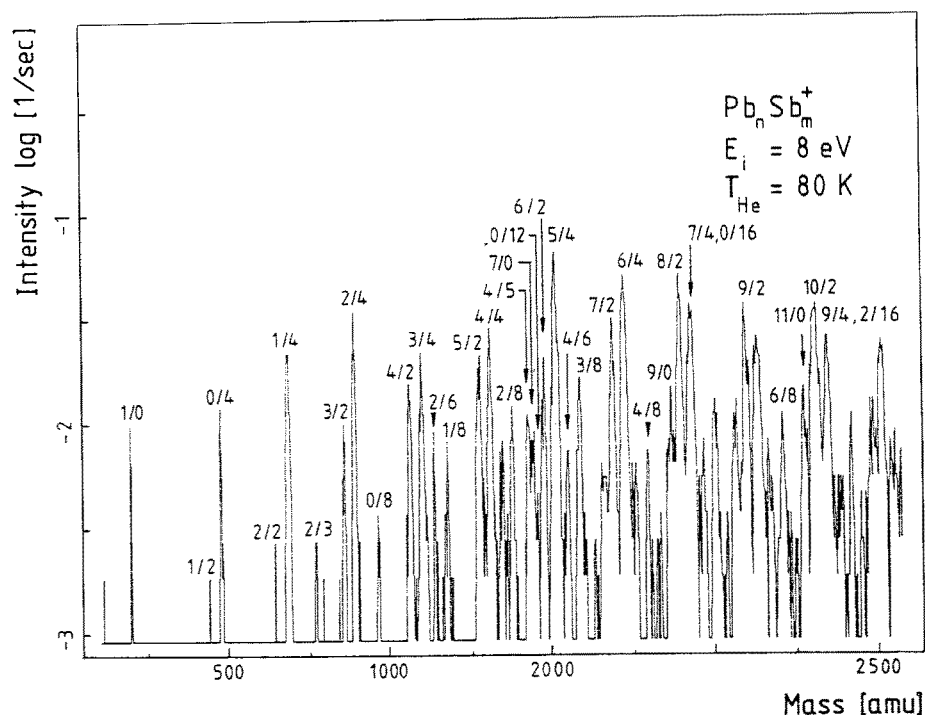
Fig. 6. Mass spectrum of Pb_nSb_m clusters and the corresponding histogram. After adsorption of one Sb_4 molecule at a Pb-clusters the reaction $Pb_n + Sb_4 \rightarrow Pb_nSb_2 + Sb_2$ occurs; dissociation onset at $n = 3$ [9]. The two black lines in the histogram increase fast with increasing electron energy and exceed at high E_i by far the other lines in the distribution. This fact is discussed in Ref. 10

Pb(solid) and 4.34 eV for Bi(solid). Therefore, the contact potential difference (considered in analogy to bulk metal-metal contacts) between the atomic adsorbates and the cluster-substrates increases with cluster size. The amount of charge transfer depends on this difference.

Besides charge transfer other effects can lead to dissociation. This is shown in the case of Bi_1, which is able to crack with high effectivity the Sb_4-molecule,

despite the ionization potentials of Bi_1 and Sb_4 are almost the same.

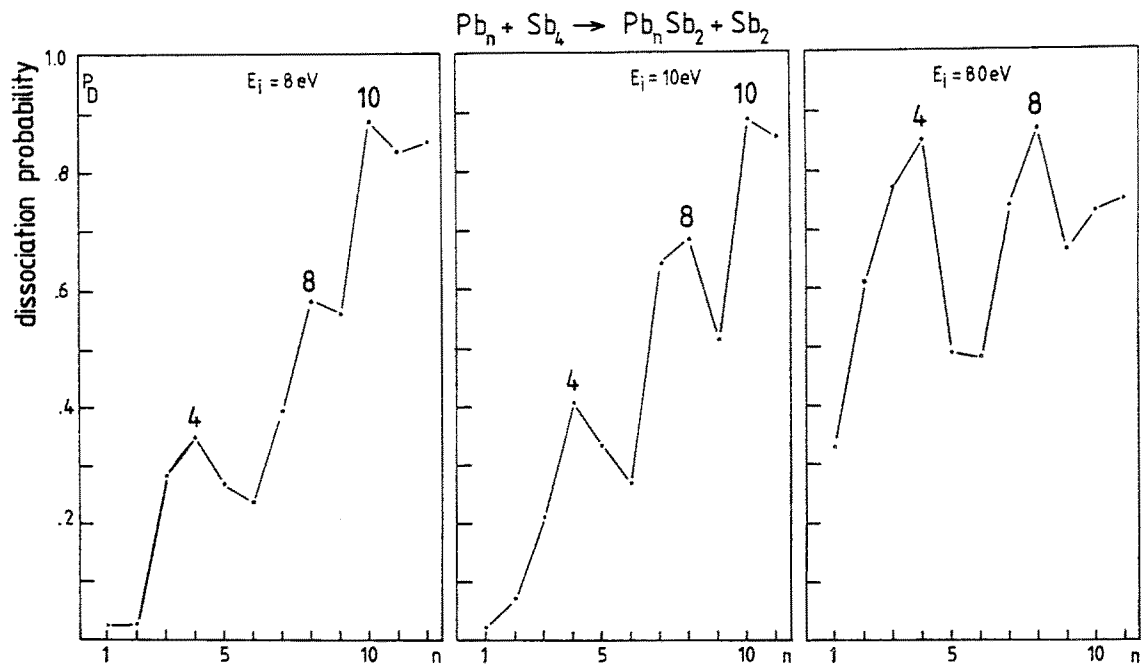$$Pb_n + Sb_4 \longrightarrow Pb_n Sb_2 + Sb_2$$

Fig. 7. Dissociation probabilities for the reaction $Pb_n + Sb_4 \rightarrow Pb_n Sb_2 + Sb_2$. The corresponding mass spectra have been taken at three different ionizing energies 8 eV, 10 eV, and 80 eV [10]
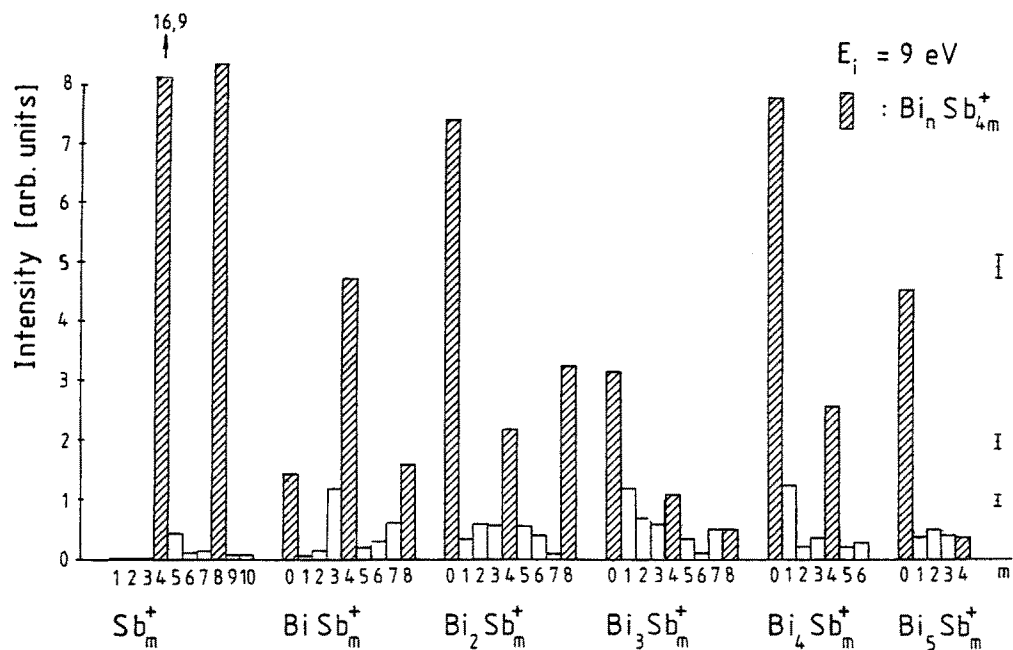

Fig. 8. Histogram for $Bi_n Sb_m$-clusters. One or two Sb_4-units are adsorbed by the Bi-clusters. Symmetrical and nonsymmetrical dissociation channels are observed; dissociation onset at $n = 1$ [9]

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