

LIQUID METAL ION SOURCE STUDY OF $\text{Bi}_n^{\text{P}^+}$ IONS ($n/p \lesssim 14$, $p \leq 4$)

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The Liquid Metal Ion Source Technique (LMIS) has already been used for studying noble metal aggregates $X_n^{\text{P}^+}$ ($X = \text{Au}$ (1) ; Cu , Ag (2)). For $p = 1$, one observes that X_n^+ aggregates with odd n values are more abundant. This property is also observed by using the Secondary Ion Mass Spectrometry Technique (SIMS) (3). The explanation of the preceding odd-even effect is that X_n^+ aggregates with odd n values have larger stabilities because they have an even number of valence electrons ($n - 1$) and, therefore, a complete level structure. This simple model also applies to X_n^{2+} noble metal aggregates where the number of valence electrons ($n - 2$) leads to the prediction of larger stabilities for even n values. Indeed, this phenomenon has been observed for Cu_n^{2+} ions (2).

In this paper we present the LMIS study of $\text{Bi}_n^{\text{P}^+}$ aggregates. The aggregates of this element are interesting since they have already been studied by two other approaches. On the one hand, they have been produced in seeded supersonic beams (4,5,6) and mass spectra or velocity distributions of Bi_n^+ clusters have been recorded. On the other hand, some $\text{Bi}_n^{\text{P}^+}$ cations have been chemically prepared (7,8) for example by the reaction between bismuth metal and dilute solutions of bismuth trichloride in liquid AlCl_3 - NaCl mixture (9). We will turn back to the results in the forthcoming discussion.

II. EXPERIMENTAL RESULTS AND DISCUSSION.

The mass spectrum and our peak identification are given Fig. 1. It can be noticed that the mass spectrum exhibits a general characteristic which can be established from the examination of the peaks for which the value of the charge

p is certain : the peaks are narrow for p = 1 and 2 and are wider for p = 3 and 4. Let us first discuss the first kind of peaks.

11.1 Singly and doubly charged aggregates. Odd-even alternations.

In most of the theoretical models (10,11,12) it is admitted that the chemical bonding is mainly due to the 5p valence electrons (three electrons per atom). By applying again the simple model given before it can be predicted that an odd-even alternation should appear, with odd-n Bi_n^+ ions (which have an even number of electron (3n-1)) more abundant.

This alternation effect is observed when aggregates are produced by the seeded supersonic beam technique (6). We observe in our spectrum a similar behaviour, except for n/p = 4. One may explain this difference by identifying the n/p = 4 Peak as being Bi_8^{2+} and not Bi_4^+ . Two arguments tend to reinforce this interpretation. Firstly, the Bi_8^{2+} aggregate is the only doubly charged bismuth cluster which has been chemically prepared (7,9) ; secondly, it is not surprising that the same effect does not occur in seeded supersonic beam experiments where the doubly charged ions are hardly produced.

Then, if we admit that the n/p = 4 peak is mainly due to Bi_8^{2+} aggregates and if we suppose that for the other peaks with integer n/p values only Bi_n^+ clusters are present one say that our mass spectrum, as supersonic seeded beam spectra, exhibits an odd-even alternation behaviour of the Bi_n^+ intensities.

11.2 Bi_n^{3+} and Bi_n^{4+} , modulo-8 periodicity.

One of the advantages of the LMIS technique is that aggregates in highly charged states are produced. We will distinguish two n/p ranges. For n/p \lesssim 5, the existence of the p = 4 charge is very unlikely because of the coulombic repulsion (13).

We will thus identify the "wide" peaks as Bi_n^{3+} aggregates and we thus obtain : Bi_4^{3+} , Bi_5^{3+} , Bi_6^{3+} , Bi_8^{3+} , Bi_{13}^{3+} . For n/p \gtrsim 5 the existence of p = 4 aggregates is no longer forbidden and we give two possible identifications for each peak. As we will see in the forthcoming discussion one of them (which is underlined) is more likely Bi_{19}^{3+} or Bi_{27}^{4+} ; Bi_{27}^{3+} or Bi_{36}^{4+} ; Bi_{23}^{3+} or Bi_{31}^{4+} (small intensity) ; Bi_{35}^{3+} or Bi_{47}^{4+} ; Bi_{36}^{3+} or Bi_{48}^{4+} ; Bi_{42}^{3+} or Bi_{56}^{4+} ; Bi_{43}^{3+} or Bi_{57}^{4+} (sometimes the two identifications correspond to two different n/p values compatible with the peak width).

If one only considers the underlined values it appears a modulo-8 periodicity for the Bi_n^{3+} . The main argument which supports the choice of the underlined values is that such periodical phenomena have already been observed for S_n^+ (14), O_n^+ (15)

and Sb_n^+ (4) (an element of the same family as bismuth) with, respectively, modulo 8, 3 and 4 periodicities.

In these last studies the periodicities are due to successive additions of neutral building blocks with respectively 8, 3 and 4 atoms in the field of a central positive charge. In our case, the repetitive building block would be Bi_8 and the observed periodicity only starts from Bi_{19}^{3+} .

Let us now compare our results on small Bi_n^{3+} to the chemical results. The only triply charged bismuth aggregate which have been prepared is Bi_5^{3+} whose structure (10) is a triangular bipyramid (D_{3h} symmetry). This aggregate is isoelectronic to the $B_5H_5^{2-}$ borane anion and has the same structure.

In our measurements we do not observe a remarkably large intensity for Bi_5^{3+} which is similar to the intensity of Bi_4^{3+} , Bi_6^{3+} or Bi_8^{3+} . The difference between chemical and LMIS results can be explained by the difference between the two production modes. In particular, the anions which are present in the chemical process seem to preferentially stabilize some Bi_n^{p+} as Bi_5^{3+} or Bi_9^{5+} (which is not observed in LMIS experiments).

Let us also give the critical sizes $n_{cri}^{(p)}(Bi)$ above which Bi_n^{p+} ions begin to be observed :

$$n_{cri}^{(2)}(Bi) = 3, \quad n_{cri}^{(3)}(Bi) = 4.$$

We note that the first value is in agreement with the value measured by Jentsch et al. (16).

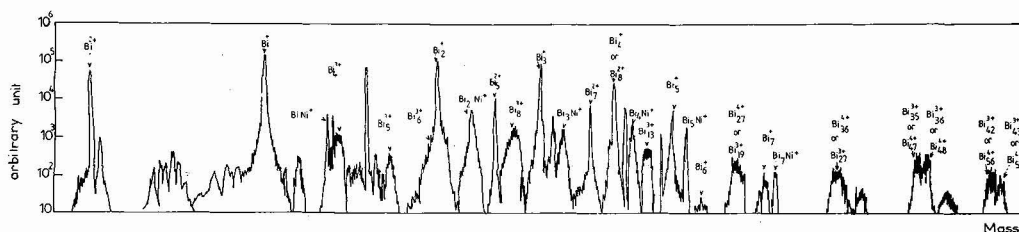


Fig. 1 - Mass spectrum of bismuth.

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