Anomalous Peaks in Mass Spectra; Effects of Pre-Analysis Dissociation and Charge Exchange Events.

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Abstract. It is common to find a considerable number of peaks in a mass spectrum that do not correspond to easily identifiable species (e.g., mass 10 and mass 80 peaks in Argon spectra). Dissociation of molecular ions and charge exchange events prior to mass analysis can account for many of these anomalies. This paper presents a general method for calculating the expected, apparent masses of these ions.

I. INTRODUCTION

It is customary to use a linear approximation of magnet current to magnetic field when calculating observed masses in a mass spectrum plot of an ion implanter. The usual form of the mass analysis equation relates analyzer current I to particle mass m, charge q, and beam extraction voltage V_{extr}:

$$I = \kappa \sqrt{\frac{m}{q} \cdot V_{extr}} \quad . \tag{1}$$

This equation assumes that ions have the same mass and charge at analysis as they had at extraction - which is the dominant process for almost all conditions of ion beam formation. Anomalous peaks arise whenever the charge state changes through ionization or electron capture and/or the mass changes through dissociation of molecular ions into component ions prior to mass analysis. The task is to find appropriate substitutions for m and q to correctly modify the mass analysis equation reflecting new, effective values for m and q,

$$I = \kappa \sqrt{\frac{m_{eff}}{q_{eff}} \cdot V_{extr}} \quad . \tag{2}$$

II. MASS ANALYSIS EQUATION

The momentum of a charged particle in a uniform magnetic field, B, is given by,

$$p = qBr \text{ [1]}. \tag{3}$$

In an ion implanter the bending radius, r, is constant and B is directly proportional to analyzer current, I, so that (3) reduces to the following relation:

$$I \propto p/q \; . \tag{4}$$

It is more convenient to express particle momentum in terms of it's kinetic energy:

$$p = mv = \sqrt{2 \cdot m \cdot E} \; . \tag{5}$$

Combining (4) and (5) and introducing the constant, κ, to absorb numerical factors and make our units cooperate, we have,

$$I = \kappa \sqrt{\frac{m}{q^2} \cdot E} \; . \tag{6}$$

In this equation, m, q and E all refer to the ion's state at analysis. To separate out the conditions at extraction from those at analysis, the subscript 'i' will be added to quantities denoting extraction states and 'f' will refer to conditions at analysis. Rewriting (6),

$$I = \kappa \sqrt{\frac{m_f}{q_f^{\,2}} \cdot E_f} \; . \tag{7}$$

The one unknown in this equation is E_f. Dissociation results in the components carrying away a portion of the original ion's energy, determined (approximately) by the mass-fraction of the component. Stated another way, after dissociation, the components continue to travel with approximately the same velocity as they had when bonded to the parent ion. The mass-fraction is simply given by, m_f/m_i so that

$$E_f = E_i \, (m_f/m_i). \tag{8}$$

The energy gain of a charged particle with charge, q, accelerated through a potential V, is E = qV. Therefore the initial energy of the parent ion is:

$$E_i = q_i V_{extr}. \tag{9}$$

Combining (7), (8), and (9), I becomes:

$$I = \kappa \sqrt{\left(\frac{m_f^{\,2}}{m_i}\right) \cdot \left(\frac{q_i}{q_f^{\,2}}\right) \cdot V_{extr}} \quad . \tag{10}$$

A nicely symmetric result!

Set $m_{eff} = (m_f^2/m_i)$ and $q_{eff} = (q_f^2/q_i)$ to obtain,

$$I = \kappa \sqrt{\frac{m_{eff}}{q_{eff}} \cdot V_{extr}}$$

as originally desired. Set $m_f = m_i$ and $q_f = q_i$ to recover the customary mass analysis equation. For purposes of evaluating energy contamination from such ions that analyze at the same rigidity to desired beams,

$$E = q_i(m_f/m_i)V_{extr} + q_f V_{PA} \qquad (11)$$

where V_{PA} denotes post-analysis acceleration.

III. EXAMPLES

A. Mass 10 and mass 80 peaks in Argon

The charge exchange mechanism that accounts for these types of beam contamination has been previously reported [2]. In this work, the spurious peaks are referred to as "Aston Bands". Suppose Ar^+ is extracted from the source and is subsequently ionized to Ar^{++} prior to analysis. The effective charge, $q_{eff} = q_f^2/q_i = 4$, therefore it would show up as a mass 10 peak. Going in the other direction, extracted Ar^{++} that is reduced to Ar^+ will be analyzed at $q_{eff} = 1/2$, or mass 80. This latter process can also occur in arsenic dimer(As_2^+) implants.

B. Phosphorus dimer in P^{++}

Assume P_2^+ is extracted and subsequently dissociates to P^+. The effective mass, $m_{eff} = m_f^2/m_i = 15.5$, is identical to P^{++}.

C. Phosphorus, mass 31. How do I count the ways?

An imminently probable, though low intensity reaction: P_4^+ dissociated to P_2^+ analyzes at mass = 31. Less probable, but interesting are two other reactions: P_4^+ ionized to P_4^{++} and P^{4+} reduced to P^{++} are also analyzed at mass = 31.

D. Masses 2.5 - 2.8, 4.0, 7.3 - 7.5 in BF_3

This investigation was partly launched by a desire to understand the very interesting grouping of peaks in BF_3 spectra. At mass 2.5, we can be seeing either $^{11}B^+$ dissociated from $^{49}BF_2^+$ or $^{10}B^{++}$ ionized from $^{10}B^+$. At 2.8 the main contributor would be $^{11}B^{++}$ ionized from $^{11}B^+$. Mass 4.0 derives from $^{11}B^+$ dissociated from $^{30}BF^+$. A host of other possible reactions fills in the 7.5 - 7.8 gap with $^{19}F^+$ dissociated from $^{49}BF_2^+$ as very likely.

IV. CONCLUSION

A straightforward equation was presented to provide a means of identifying unusual peaks in mass spectra and also to provide a means of evaluating potential contaminants in standard ion beam species. This process can be easily adapted to a spreadsheet for rapid calculation of a very broad range of possible reactions. A caveat to consider is that anomalous peaks are unlikely to be probable if their parent ions are not present as a primary peak in the mass spectrum.

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