Electron Capture by Gaseous Ions in Mass Spectrometers

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Summary An ion with mass twice that of the molecular ion, M^{+}, is attributed to the electron capture by the doubly charged molecular ion, $M^{2+} + e \longrightarrow M^{+}$, in the field-free region of a mass spectrometer.

THE 70 ev mass spectrum of mercury consists of the peaks due to Hg^{+}, Hg^{2+}, and Hg^{3+} with their characteristic isotopic patterns as illustrated in the Figure (a). (The weak peaks due to Hg^{3+} are not shown). Recently, we have observed a group of weak peaks at *m/e* 396—408 with the isotopic pattern of monatomic mercury [*cf.* Figure (a)]. This unique isotopic pattern immediately rules out the possibility that the ions are due to Hg_2^{+}, which might have been generated from an ion–molecular reaction. For a reaction $m_1^{x+} \longrightarrow m_2^{y+}$ occurring in the field-free region of a mass spectrometer, the apparent mass of the product ion will be $m^* = m_2^2 x/m_1 y^2$. Based on this equation and the relative abundances of mercury isotopes, the calculated masses and relative intensities of the ions generated from the reaction, $Hg^{2+} + e \longrightarrow Hg^{+}$, in the field-free region are exactly what we have observed. The electrons are believed to be the secondary electrons produced when the ion beam strikes the two slits defining the field-free region. Similar results were also obtained for nitrogen [Figure (b)]. A weak ion, *m/e* 56, was detected. Therefore, the peak at *m/e* 14 is due to two isobaric ions, N^{+} and N_2^{2+}. The double ionization potential of $^{14}N^{15}N$ was measured as 43·5 ± 0·3 ev.[1] However, in this particular case, we cannot rule out entirely the presence of the ion N_4^{+}, possibly generated from an ion–molecular reaction. The electron capture by gaseous ions in the ion-source might be to a great extent due to the high densities of electrons and ions present. However, this phenomenon has not been discussed previously.

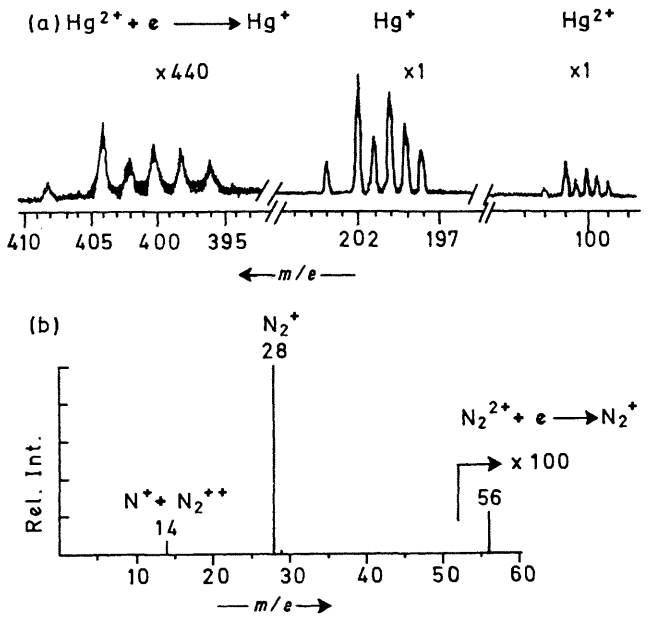

FIGURE. *Mass spectra of* (a) *mercury and* (b) *nitrogen*

The mass spectrum of mercury was recorded with an Atlas CH4B mass spectrometer with the source chamber pressure $< 10^{-7}$ Torr. The mass spectrum of nitrogen was recorded with a standard 90° magnetic-sector mass spectrometer.

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[1] F. H. Dorman and J. D. Morrison, *J. Chem. Phys.*, 1961, **35**, 575.