Experimental Investigations of Trimer Ion Contributions in the Low Resolution Mass Spectrometry of Hydrogen Isotope Mixtures

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This paper reports on some preliminary experimental results of a work in progress regarding a problem involving the quantitative analysis of hydrogen isotopes by mass spectrometry of low resolution: the triatomic (trimer) ions interferences with the isotopic hydrogen species having the same mass/charge. These results indicate that, in complex mixtures of hydrogen isotopes, trimer ions are strongly affected by the presence of other species, and a new approach that takes into account the destruction mechanism of trimer ions is necessary for a proper determination of their contributions.

(Received September 20, 2012; Accepted October 1, 2012; Published November 10, 2012)

Introduction

One of the main issues in the quantitative analysis of hydrogen isotopes gas mixtures by mass spectrometry of low resolution is the interferences of triatomic (also named trimer) ions with ions of isotopic species of molecular hydrogen having the same mass/charge (*e.g.* H_3^+/HD^+ , $\text{H}_2\text{D}^+/[\text{D}_2^+ + \text{HT}^+]$, $\text{HD}_2^+/\text{DT}^+$, and so forth). The contributions of these trimer ions to the total ion-currents measured at the m/z ratios of interest have to be properly determined and subtracted as a condition for obtaining reliable analysis results for hydrogen isotopic composition. The pathway for the production of trimer ions in the electron impact ion source is the reaction between molecular hydrogen species and its ions (*e.g.* reaction $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}\cdot$).¹ In hydrogen isotope ratio mass spectrometry (IRMS, conventional or modern), the main problem is the interference of H_3^+ with HD^+ at mass 3 ion-current.^{2–4} According to the above reaction, the production of H_3^+ is proportional to both the abundance of H_2^+ and the H_2 partial pressure. Under linear operation conditions of the mass spectrometer, the abundance of H_2^+ is proportional to the partial pressure of H_2 gas in the ion source. Thus, the production of H_3^+ is proportional to the second power of the H_2^+ abundance. The result is that for natural (or close to natural) molecular hydrogen the total current measured at mass 3 is:^{3–5}

$$I_3 = I_{\text{H}_3^+} + I_{\text{HD}^+} = KI_2^2 + R^*I_2, \quad (1)$$

where the proportionality factor, K , is “the H_3 factor”; I_2 and I_3 , total ion-currents measured at mass 2 and 3, respectively; I_{HD^+} and $I_{\text{H}_3^+}$, ion-currents due to the HD^+ and H_3^+ ions, respectively; and R^* , measured isotopic ratio, HD/H_2 . The H_3 factor, K , is usually determined by measuring I_3 over a range of H_2 pressures in the ion source, and using the least-squares regression of the linear expression of the ratio I_3/I_2 as a function of I_2 , as derived from Eq. (1).^{3–6} This is the common approach used in IRMS for natural, or close to natural, deuterium abundance. However, in

complex mixtures of hydrogen isotope species, these equations do not provide a realistic description of the trimer ion contributions, as the following experimental results demonstrate.

Experimental

The experimental results reported here were obtained with a commercial Quadrupole Mass Spectrometer (QMS) of unit resolution, Hiden Analytical HPR20, intended to replace the current gas-chromatograph used to monitor hydrogen isotope species in the process gases to the water detritiation facility from ICSI Rm. Valcea, Romania. The inlet system utilises a one-metre long capillary sampling line that is connected directly to the ion source, and is bypass pumped. Bypass pumping provides rapid evacuation of the inlet system volume; it also, with the aim of a micrometric control valve, allows the user to control the pressure in the ion source. A cold cathode (Penning) gauge is fitted to monitor the UHV housing pressure. The operation parameters of the (gas-tight) ion source were: cage voltage, 5 V; focus voltage, –110 V; electron energy, 70 V; and emission current, 1 mA.

The samples used were chemically pure hydrogen (with natural content of deuterium) and deuterium (with about 0.2% content of hydrogen), and laboratory-prepared mixtures (by partial pressure method of mixing) of hydrogen and deuterium with nitrogen gas. The sample IDs and the corresponding approximate proportions are as follows: HD-1 (50% H_2 , 50% D_2), HN-1 (75% H_2 , 25% N_2), HN-2 (50% H_2 , 50% N_2), HN-3 (30% H_2 , 70% N_2), HN-4 (10% H_2 , 90% N_2), DN-1 (80% D_2 , 20% N_2), DN-2 (50% D_2 , 50% N_2), DN-3 (30% D_2 , 70% N_2), and DN-4 (10% D_2 , 90% N_2).

Results and Discussion

Because the formation of D_3^+ ions occurs in pure deuterium gas through reactions between D_2 neutrals and its ions, the ion-current measured at m/z 6 should be:

$$I_6 = I_{D_3^+} = K' I_4^2. \quad (2)$$

A first interesting result has been obtained by analysing samples D₂ and HD-1 at different values of the total pressure in the UHV housing (from ultimate vacuum up to about 10⁻⁷ Torr). Two quite different curves, which describe the dependences of I_6 on I_4 for samples D₂ (points marked with “x”) and HD-1 (points marked with “+”), respectively, on the same range of D_2 partial pressure, can be viewed in Fig. 1(b), indicating that a great admixture of hydrogen (~50%) in deuterium gas leads to a reduction of D_3^+ ions. This observation contradicts Eq. (2), and suggests that the K' factor, determined by using pure deuterium, cannot be used to properly correct the mass 6 ion-current for measuring low contents of T₂ in D₂/H₂ mixtures.

Since similar observation on how the H_3^+ is influenced by a great admixture of deuterium was not possible, due to the relatively high content of HD (about 0.2%) in the deuterium gas, two sets of H₂/N₂ and D₂/N₂ mixtures (described above) were prepared and analysed in order to verify if nitrogen is influencing the trimer ions H_3^+ and D_3^+ . The results of the measurements performed for the two sets of mixtures at different values of the total pressure are graphically presented in Figs. 1 (a) and 1(b), respectively. Both sets of results are similar, showing that the trimer ion-current contributions are very strongly related not only to the abundance of the parent species, but also to the abundance of the mixing species (nitrogen). This result could be explained by the destruction of low-energy trimer ions in reactions with neutral nitrogen molecules.⁷⁻¹⁰ However, this process is not described by Eqs. (1) and (2). Also, according to these equations, the ion-current ratios, I_3/I_2 and I_6/I_4 , should not depend on the nitrogen partial pressure, and should be constant at constant partial pressures of H₂ and D₂ (*i.e.* constant values for I_2 and I_4), respectively. On the contrary, by measuring the two sets of samples for I_2 and I_4 , respectively, fixed at 4×10^{-11} A ($\pm 5\%$), it can be observed (Fig. 2) that the two current ratios decrease with the increase of nitrogen partial pressure according to hyperbolic functions of form $y = 1/(a + bx)$.

In Fig. 3, which presents two spectra acquired at the same D₂ partial pressure for samples D₂ (triangles with dashed line) and DN-4 (circles with solid line), the reduction of the trimer ion-current contribution as an effect of a nitrogen admixture can also be seen very clearly at m/z 5 and 6 for HD_2^+ and D_3^+ ,

respectively. Thus, another useful observation is that the mixing of hydrogen isotope samples with nitrogen gas could be used as a more efficient way to reduce the trimer ion contributions, rather than the IRMS popular option of pressure reduction.

The behaviour of trimer ions in the presence (of high concentration) of other gases is not a serious problem on the D/H measurements by IRMS techniques because relatively pure hydrogen gas is loaded into ion sources. However, when complex mixtures of hydrogen isotopes (possibly together with other gases such as nitrogen, in particular cases of purging gases, or glove-boxes environment, *etc.*) are analyzed by using a QMS, the equations used in the IRMS approach to determine the trimer ion contributions are not appropriate (as the experimental results presented here show). Thus, not only the formation, but also the destruction mechanism of trimer ions had to be considered in these cases. A new (and more reliable) theoretical model and its experimental verification will be presented in a next paper.

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Fig. 2 Variation of the ion-current ratios, I_3/I_2 and I_6/I_4 , on I_{28} for the two sets of samples analysed, respectively, with I_2 and I_4 established at 4×10^{-11} A.

Fig. 1 Ion currents measured at different values for the total pressure in UHV housing: (a) I_3 as function of I_2 , for H₂/N₂ mixtures, (b) I_6 as function of I_4 , for D₂/H₂ and D₂/N₂ mixtures.

Fig. 3 Two mass spectra recorded for samples D₂ and DN-4 for the same value of the ion-current measured at m/z 4 (about 4×10^{-11} A).

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