

Metastable Ions in the Mass Spectrum of Uranium Hexafluoride

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Mass spectrometry of metastable ions is extensively used in organic chemistry for gaining extra information on the composition of complex mixtures and the molecule structure [1, 2]. Metastable ions arise when some of the ions (including fracture ions) generated in an ion source are in the excited state with a lifetime comparable to the time of ion transit between the source and the collector. A parent (metastable) ion with a mass M_1 disintegrates following the reaction



to produce a daughter ion M_2^+ . In doing so, the parent ion changes its mass, energy, and, as a consequence, trajectory curvature in a magnetic field.

Mass spectra of uranium hexafluoride samples with the natural isotopic composition were taken with an MI-1201 AGM mass spectrometer operating in the ion counting regime. The mass spectrum of ions with masses ranging from 220 to 355 is shown in Fig. 1. The magnified region of the highest peak corresponding to metastable ions with a mass number of 296 is depicted in Fig. 2. A metastable ion peak can easily be distinguished by its width. For instance, the halfheight resolutions of the mass-292 and mass-296 peaks are $R_{50} = 1116 \pm 17$ and 586 ± 1.6 , respectively.

The peaks associated with masses of 258, 277, 296, and 315 (produced by the parent ions with masses of 295, 314, 333, and 352, respectively) were also identified. For this purpose, the spectrometer mass scale in Fig. 1 was calibrated with the reference masses of UF_6 ion fragments. The corrections ΔM to the peak positions measured by the mass spectrometer are well approximated by a parabola (Fig. 3). The standard error of approximation was 2.7 mu ($1 \text{ mu} = 10^{-3} \text{ u}$).

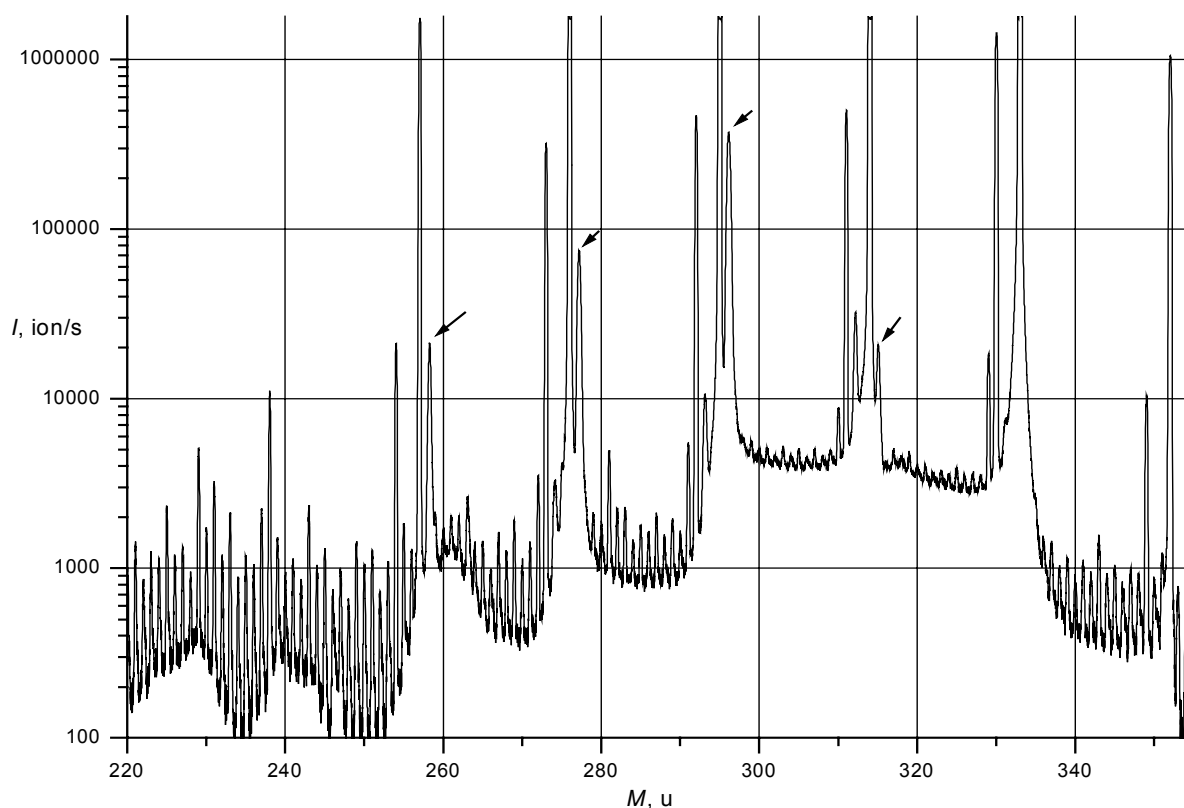


Fig. 1. Mass spectrum of UF_6 .

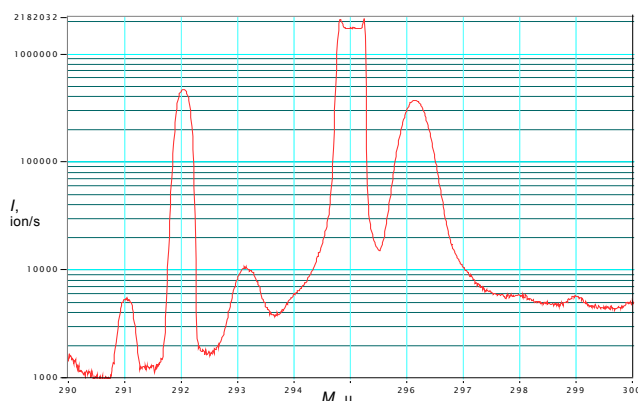


Fig. 2. Fragment of the mass spectrum for UF_6

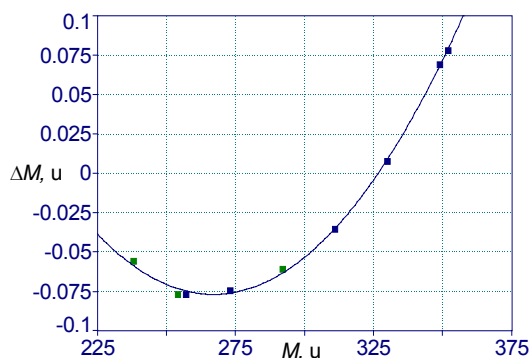


Fig. 3. Correction curve for the mass scale.

The corrected masses of the metastable daughter ions were compared with the calculated (apparent) masses (Table 1). The calculation was carried out by the formula

$$M_{\text{cal}} = \frac{M_2^2}{M_1}, \quad (2)$$

This formula assumes that disintegration products go on moving with the same velocity as a parent ion and that the parent ion disintegrates on its way between the ion source and the entrance to the magnetic field of the analyzer (field-free space).

The good agreement between the calculated and measured masses of the metastable ions (the discrepancy is ≈ 0.01 u) means that the lines broadened are correctly identified as belonging to the daughter metastable ions.

The trajectory of daughter metastable ions and, as a result, the position of the corresponding peaks in the mass spectrum depend on the region of disintegration of a parent metastable ion. This is illustrated with the disintegration $333^+ \rightarrow 314^+ + 19^0$ (Table 2).

From this table, it follows that the ions disintegrated in the magnetic field are distributed over the mass range between 296 and 333, causing the substantial increase (approximately, five times) in the background ion current for masses higher than 296 (Fig. 1). Also, the height of the metastable ion peaks correlates with the background ion current due to these peaks. This dependence is nearly linear (up to 30%) if we assume that the contribution of the scattered ion current 150 ions/s to the background ion current is constant. The mass spectra with the starting and corrected mass scales are available from <ftp://www.mp.dpt.ustu.ru/spectr> (files Spectr 1 and Spectr 2, respectively).

Table 1. Comparison between the measured and calculated masses of the daughter metastable ions

M_m, u	M_{cal}, u	$M_m - M_{\text{cal}}, \text{mu}$	Error, mu
258,2846	258,2725	12,0	$\pm 1,5$
277,2079	277,1969	11,0	$\pm 1,6$
296,1417	296,1298	11,9	$\pm 1,8$
315,0728	315,0697	3,1	$\pm 1,7$

Table 2. Position of the peak for $^{238}\text{UF}_4^+$ the daughter ion ($M = 314$) in the mass spectrum vs. site of disintegration of the $^{238}\text{UF}_5^+$ metastable ion

Site of $333^+ \rightarrow 314^+ + 19^0$ disintegration	Position in spectrum
Ionization chamber	314
Between ionization chamber and exit slit of ion source	314–296
Between exit slit of ion source and entrance to magnetic field	296
Magnetic field	296–333
Exit from magnetic field	333

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1. J.H. Beynon, *Mass Spectrometry and Its Applications in Organic Chemistry* (Elsevier, Amsterdam, 1960; Khimiya, Moscow, 1964).
2. J. Chapman, *Practical Organic Mass Spectrometry* (Wiley, Chichester, 1985; Mir, Moscow, 1988).