

BRIEF
COMMUNICATIONS

Metastable Ions in the Mass Spectrum of Uranium Hexafluoride

B. A. Kalinin, V. E. Atanov, and O. E. Aleksandrov

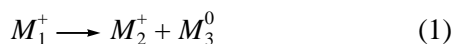
Ural State Technical University, ul. Mira 19 Yekaterinburg, 620002 Russia

e-mail: kalinin@dpt.ustu.ru

Received October 15, 2001

Abstract—A high content (about 0.3%) of metastable ions is detected in the mass spectrum of uranium hexafluoride (UF_6). The apparent masses of the metastable ions found from the masses of UF_6 fragment ions, which were taken as references are close to values predicted (the discrepancy is no more than 0.015 u). It is shown that these ions are responsible for the background current in a wide mass range. The lifetime of a UF_5 metastable ion with a mass of 333 is estimated. © 2002 MAIK “Nauka/Interperiodica”.

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. In practice, an ion produced when a truly metastable ion disintegrates on its way between the source and the collector is often also called metastable [2, p. 147]; however, such terms as parent ions and daughter ions are more appropriate here [3]. 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.¹ The mass spectrum of ions with masses ranging from 230 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.

The ion current is plotted on the ordinate in ions/s. The tops of the peaks for ions with mass numbers of 333, 314, 295, and 276 (Fig. 1) are distorted because these peaks go beyond the upper limit of the dynamic range of the ion counter. The mass spectrum was taken for 3.5 h at an ionizing voltage of 50 V, an emission current of 0.1 mA, an accelerating voltage of 5 kV, a sweep

pitch over the mass scale of 0.01 u, and an integration time per point of 1 s. A metastable ion peak can easily be distinguished by its width. For instance, the half-height 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 ($1 \text{ mu} = 10^{-3} \text{ u}$).

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

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

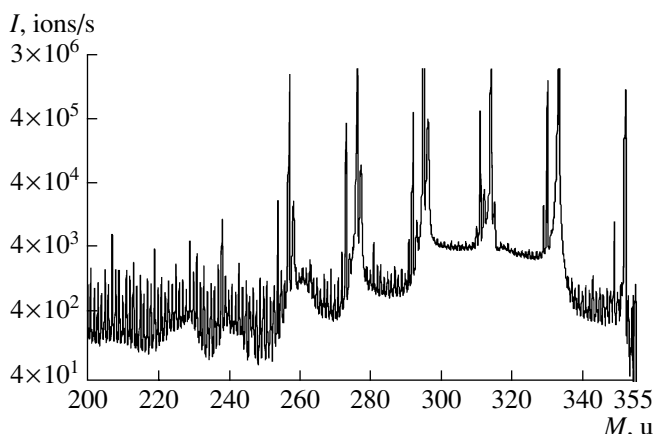


Fig. 1. Mass spectrum of UF_6 .

¹ An MI-1201 AGM single-focusing sector mass spectrometer is provided with a secondary emission multiplier (SEM) and a counter of pulses due to ions striking the SEM collector.

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 values measured exceed those calculated, as has been observed earlier [1, p. 259], possibly because of a strong electric field gradient at the entrance slit of the mass spectrometer, which influences the lifetime of the metastable ions.

On the other hand, 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 elevation of the background ion current near $M = 262$ can be explained by the disintegration $333^+ \rightarrow 295^+ + 38^\circ$ with the formation of ions with an apparent mass of 261.4. Similarly, the background ion current near $M = 241$ is related to the disintegration $314^+ \rightarrow 276^+ + 38^\circ$ with the formation of ions with an apparent mass of 242.6.

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 $333^+ \rightarrow 314^+ + 19^\circ$ (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 spectrum shows that the background ion current decreases, for instance, in the range between 315 and 329 because of the disintegration of the metastable ions (the decrease in their number) when they move in the magnetic field. A feature of the metastable ion disintegration in the ion source is that the masses of the ions decrease as the site of disintegration shifts toward the exit slit. As a result, the background ion current drops more slowly in the range between 296 and 310.

The dimensions of the ion channel in the mass spectrometer are as follows: the distance from the exit slit of the ion source to the entrance to the magnetic analyzer is 39.5 cm; the ion path length in the magnetic field (with the stray field neglected), 29 cm; and the distance between the exit of the magnetic analyzer and the ion collector, 42 cm. Knowing the dimensions of the ion channel, one can estimate the lifetime of the metastable ions.

With these dimensions and an accelerating voltage of 5 kV, the ion transit time through the channel is 20 μ s. The lifetime of a metastable ion is expected to be of the same order of magnitude. This value for the UF_5

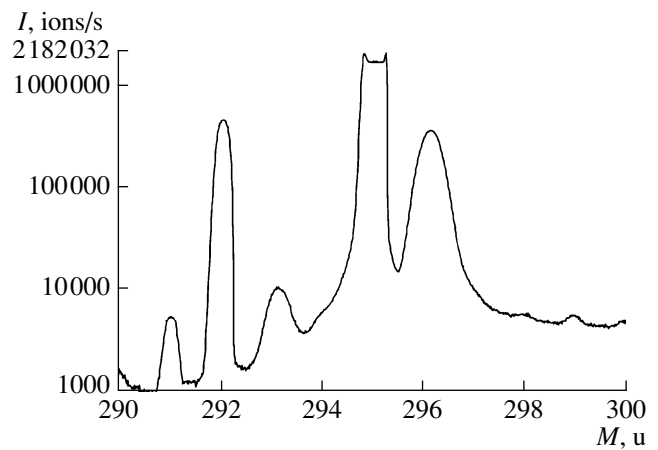


Fig. 2. Fragment of the mass spectrum for UF_6 .

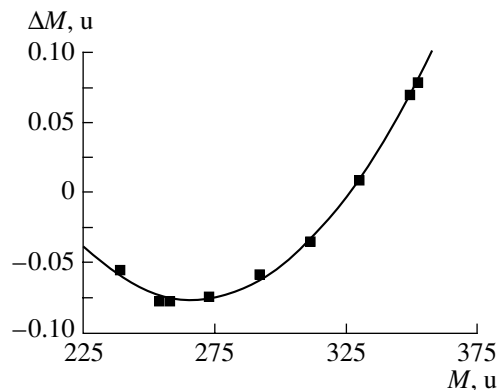


Fig. 3. Correction curve for the mass scale.

metastable ion ($M = 333$) can be estimated more accurately from the background ion current varying from 4×10^3 to 2.9×10^3 ions/s in the mass range between 314 and 326. Since the total channel length in the magnetic field is covered by ions of masses 333–296, the travel of ions with masses of 326–314 is equal to $(29/37) \times 12 = 9.4$ cm and the transit time for this length is $t = 1.7$ μ s. Then,

$$\tau = \frac{t}{\ln \frac{N_1}{N_2}} = \frac{1.7}{\ln \frac{4}{2.9}} = 5.3 \mu\text{s}.$$

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

M_m, u	M_{cal}, u	$M_m - M_{cal}, \mu u$	Error, μu
258.2846	258.2725	12.0	± 1.5
277.2079	277.1969	11.0	± 1.6
296.1417	296.1298	11.9	± 1.8
315.0728	315.0697	3.1	± 1.7

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

Site of $333^+ \longrightarrow 314^+ + 19^0$ disintegration	Position in mass 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

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).

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education of the Russian Federation (grant no. 05.01.038).

REFERENCES

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).
3. A. A. Polyakova, *Molecular Mass Spectrometric Analysis of Organic Compounds* (Khimiya, Moscow, 1983).

Translated by B. Malyukov

SPELL: ok