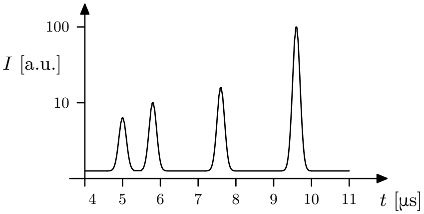
Problem VI.2 ... time-of-flight spectrometer

3 points; (chybí statistiky)



One way to determine the composition of a sample is mass spectrometry. Consider a time-of-flight spectrometer, in which particles (atoms and molecules) are initially ionized by removing an electron and then accelerated by a voltage of $U = 10\,\mathrm{kV}$*. They then travel at a constant velocity through the spectrometer body of length* $d = 2.0\,\mathrm{m}$ *until they reach the particle detector, where their count* I *is recorded as a function of the time of flight* t*. During ionization, a molecule may also break into several fragments, which then travel to the detector. The graph shows such a measured dependence for a known triatomic molecule made of two elements. Estimate which atoms or molecules correspond to each detected particle cluster and determine the original molecule they initially formed. Assume all charged particles entered the spectrometer body at the same time.*

Bonus: *With a better, more precise detector, additional particles were detected at times* $9.7\,\mathrm{\mu s}$ *and* $6.7\,\mathrm{\mu s}$*. How would you explain the presence of these particles if the only source was the same molecule as in the first part of the problem?*

Jarda is studying for state exams.

The difference in the particles' time of flight is caused by their different masses. All particles have the same kinetic energy $E_\mathrm{k} = Ue$, where U is the accelerating potential e and e the elementary charge the elementary charge produced by ionization. However, their masses (and thus velocities) differ. Additional fragment peaks appear because further fragmentation can occur during ionization. Electrons in the ionization region can remove multiple electrons from a molecule or even knock off entire atoms; any ionized piece smaller than the original particle is called a fragment. To calculate the velocity of each fragment, we use the kinetic energy formula

$$v = \sqrt{\frac{2Ue}{m}}\,,$$

where m is the mass of the fragments. The time of flight in the spectrometer will be

$$t = \frac{d}{v} = d\sqrt{\frac{m}{2Ue}}\,,$$

from this, we can express the fragment mass in atomic units ($m_u = 1.67 \cdot 10^{-27 kg}$) as

$$m_\mathrm{m} = \frac{2Ue}{d^2 m_u} t^2\,.$$

For the times $5.0\mathrm{\mu}s$, $5.8\,\mathrm{\mu}s$, $7.6\,\mathrm{\mu}s$, and $9.6\,\mathrm{\mu}s$, we obtain the fragment masses of 12, 16, 28 and 44, respectively. The interpretation of the mass spectra can be complex; however, the problem statement states that the original molecule had three atoms and was composed of two elements. To satisfy these conditions, the fragments with masses 12 and 16 must be the original atoms. Known atoms with such masses correspond to carbon ${}^{12}_{6}\mathrm{C}$ and oxygen ${}^{16}_{8}\mathrm{O}$. The fragment with a mass of 28 therefore corresponds to CO^+ and the one with a mass of 44 corresponds to the singly charged ${\mathrm{CO}_2}^+$ ion. The original molecule is therefore CO_2.

Bonus Problem

The fragments detected at time 9.7 µ*s* have a mass of 45, one mass unit greater than the standard $^{12}\mathrm{C}^{16}\mathrm{O}_2$ molecule. We know that we are dealing with a pure gas; therefore, only carbon and oxygen are present. The mass shift arises from an isotopic substitution. Although the oxygen isotope $^{17}\mathrm{O}$, which has one neutron more than the standard $^{16}\mathrm{O}$, occurs naturally, the heavier carbon isotope $^{13}\mathrm{C}$ is more abundant. Thus, the signal at 9.7 µ*s* corresponds to the molecule $^{13}\mathrm{C}^{16}\mathrm{O}_2$.

The particles recorded at the time 6.8 µ*s* correspond to a mass of 22, which does not match any expected isotope combination of the elements present. It is, however, noteworthy that it is half the mass of $^{12}\mathrm{C}^{16}\mathrm{O}_2$. The number 22 therefore does not correspond to any real mass of these fragments, but to an entire (doubly charged) molecule $(^{12}\mathrm{C}^{16}\mathrm{O}_2)^{2+}$. Such ions gain twice the kinetic energy, so they appear in the spectrum as if they had half the mass. Of course, double ionization is much less probable than a single ionization; hence this signal is typically less intense.

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