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Investigation of ion cluster formation in a pulsed ion mobility spectrometer operating in the negative mode

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ABSTRACT

Ion mobility spectrometry (IMS) is a well-known technique for fast trace gases detection. Employing atmospheric pressure chemical ionization in IMS, ion clusters, e.g. protonated monomer or proton bound dimer analyte ions such as $MH^+(H_2O)_n$ or $M_2H^+(H_2O)_n$ form in the positive mode, where the chemical ionization is based on positively charged reactant ions $H^+(H_2O)_n$. In the negative mode, where the ionization is based on negatively charged reactant ions $O_2^-(H_2O)_n$, similar cluster formation is possible but less common. In this paper, we investigate 2-chlorophenol, formic acid and toluene-diisocyanate as single substances and in mixtures, showing their different behavior regarding the formation of symmetric and asymmetric clusters and thus the presence and absence of additional peaks in the ion mobility spectra. Quantum-chemical calculations regarding the stabilization energy can explain the absence of certain cluster signals quite well when based on the assumption of ionization by electron capture in contrast to the typically expected ionization by proton abstraction.

1. Introduction

Ion mobility spectrometry (IMS) offers advantages over other gas analyzers due to its small size/portability, fast response time in the range of a few seconds and very high sensitivity with detection limits in the lower ppbv range. Consequently, it has been applied with great success in the detection of trace gases in security applications such as the detection of explosives, chemical warfare agents and illegal drugs [1]. Modern applications, especially in combination with other techniques (i.e. mass spectrometry and/or gas chromatography) aim for more analytical tasks such as structural analysis [2], where IMS can provide additional information by measuring the mobility of an analyte. However, the most striking disadvantages of this technique are its low resolving power (commercial devices have a resolving power in the range of 30–60) and, when atmospheric pressure chemical ionization (APCI) is used, the dependence of the peak intensity on the interaction of different analytes present in the ionization region. Thus, IMS devices work best when only a small number of analytes is present, or at the best just one analyte. If more than one analyte is present in a gas sample, cross sensitivity effects are possible. These can be an intensity

reduction of a certain analyte peak or even its complete discrimination (benzene and toluene are a well-known mixture, where the benzene peak completely disappears in the presence of even relatively low concentrations of toluene [3]). Another possibility is the appearance of additional peaks due to cluster formation.

Cluster formation is well-known in the positive mode of IMS with APCI sources. Here, protonated water clusters (free electrons, generated by an ionization source, lead in a cascade of chemical reactions – especially involving atmospheric N_2 – to the formation of positively charged reactant ions) ionize the analyte [1]. The reactant ions eventually ionize neutral analytes forming positive analyte ions. Additionally, depending on the concentration, proton-bound dimers can be formed with neutral analytes. Thus, one analyte typically leads to two peaks in the spectrum; at higher concentrations the monomer peak usually disappears and only the dimer peak is observed. If more than one analyte is present, an additional proton-bound asymmetric dimer consisting of one molecule of each analyte can form and thus lead to another peak apart from monomer and dimer peaks [4,5]. The IMS spectrum of two or more analytes thus can become quite complex. Fig. 1 is an example of three substances recorded in the positive mode, i.e. dimethyl formamide (DMF), ethyl methyl ketone (EMF) and diisobutylketone (DIBK). In addition to the reactant ion peak (RIP), there are three peaks for each substance, three peaks for the corresponding symmetric dimers (two of them being very close to each other) and

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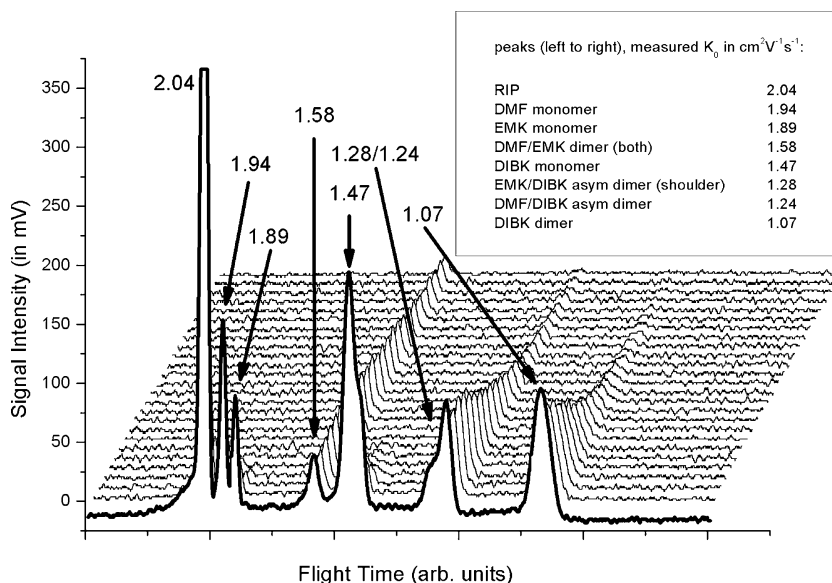
Fig. 1. Example for the complexity of an IMS spectrum with three substances recorded in the positive mode: dimethylformamide (DMF), ethyl methyl ketone (EMK) and diisobutyl ketone (DIBK). For DMF and EMK the dimers have almost the same flight time but are still distinguishable, while their asymmetric dimer is not visible.

two of the three possible asymmetric dimer peaks. In this example, three substances thus lead to eight analyte peaks. Therefore, a simplification of such a complex spectrum, especially when used to analyze unknown mixtures, is very useful. One elegant method, also shown in Fig. 1, is using pulsed ionization followed by a delay time before ion detection. During such a delay ions recombine, and the total ion intensity decreases over time. The longer the delay time the stronger the signal decrease. As already described in previous publications, dimer signals decay much slower than monomer signals and can thus be discriminated against monomer peaks. The ion mobility spectra of the waterfall graph in Fig. 1 were recorded by stepwise (100 μs) increasing the delay time. After a delay of 1 ms only one dimer peak is present. The dimer peak with the highest proton affinity usually shows the slowest decay; here this is DMF (almost not visible in the beginning due to a very similar ion mobility as compared to the EMF dimer peak, which shows a faster decay with increasing delay leading to a slight shift of the peak).

In negative mode where analyte ions are formed by electron transfer or electron capture, cluster formation is observed less frequently. The stabilization of a cluster is not achieved via protons but rather large negative ions, such as Cl^- or Br^- if present as reactant ions (e.g. dichlorophenol [6] or fluorophenols with Cl^- or Br^- as reactant ions [7], or enflurane and isoflurane with Cl^- as reactant ions [8]). Another cluster that has been observed with chlorophenols using liquid chromatography followed by electrospray ionization in an ion mobility spectrometer (LC/ESI/IMS) results from adduct formation by an analyte anion and a neutral analyte molecule, i.e. a phenoxide-chlorophenol adduct [9]. With LC/ESI/IMS also asymmetric clusters have been observed [9] (i.e. acetic acid-phenoxide adducts, the acetic acid being a left over of a chromatography step). Thus, as in the positive mode cluster formation can also lead to several peaks in the negative ion mobility spectrum, albeit less common.

For the positive mode, we have shown in previous publications how pulsed ionization can be used to discriminate dimer signals against monomer signals and help to simplify a complex spectrum of an analyte mixture [10]. In this paper, we describe a similar investigation for the negative mode. After a short description of the experimental setup we will present ion mobility spectra of mixtures of formic acid (FA), 2-chlorophenol (2CP) and toluene-diisocyanate (TDI) recorded with a pulsed ionization source. The

focus of this paper is on negative ion cluster peaks and their behavior at increasing delay times between ion formation and ion detection. Finally, we will apply quantum chemical calculations of the cluster stabilization energy using standard density functionals (B98 and B3LYP) with corresponding basis sets (6-311++G(3df,3dp) and 6-31(d)) in order to try to explain the presence and absence of certain cluster signals.

2. Experimental

The setup has been intensively described in previous publications [11–13] so that we just give a short summary. We use a modified Draeger Ion Mobility Spectrometer GSM consisting of a 4-mm long reaction region, a 5.5-cm long drift region and a 0.5-mm long collector region. The device is operated at a temperature of 340 K. At a frequency of 30 Hz, an injection field is used after pulsed ionization to inject the ions from the reaction region into the drift region, where a permanent field of about 200 V/cm accelerates the ions towards the collector region. Before ionization, a small field of 3 V/cm in the reaction region prevents ion losses into the drift region. Once accelerated into the drift region, the ions collide on their way through the drift region with air molecules (drift tube and reaction region are at atmospheric pressure) of an air flow of 200 ml/min directed opposite to the ions' motion. The flow rate is controlled by a mass flow controller. In the collector region the ions experience a field of 1000 V/cm moving the ions to the detector, which is a simple Faraday cup.

A pulsed electron gun emits free electrons that lead to the formation of reactant ions in the reaction region. The electron gun has been improved by replacing the original filament that initially emits electrons by glow discharge with a new barium electrode, so that now sufficiently strong electron pulses can be generated with a pulse duration of only 0.2 μs at a voltage of 4.5 V supplied to the filament. The potential difference accelerating the electrons is set to 7 kV so that their average kinetic energy is similar to that of beta-radiation emitted from radioactive tritium sources.

Different analyte concentrations are generated by mixing dry air (water concentration at 292 K below 200 ppbv, dew point of 181.1 K) with a gas mixture composed of dry air and analytes (generated via gas evaporation in a permeation oven into a constant air flow of 100 ml/min). The concentrations have been verified with an