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Distinction of Structural Isomers of Benzenediamin and Difluorobenzene by Means of Chirped Femtosecond Laser Ionization Mass Spectrometry

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Abstract: Structural isomers of disubstituted benzenes are difficult to distinguish with most mass spectrometric methods. Consequently, conventional concepts for the distinction of isomers are based on coupling mass spectrometry with a chromatographic method. As an alternative approach, we propose the combination of femtosecond laser ionization with time-of-flight mass spectrometry (fs-LIMS). The possibility of systematic tailoring of fs-laser pulse shapes opens access to a multidimensional analytical technique capable of distinguishing structural isomers of the title molecules.

Keywords: chemical analysis of isomers; chirp; femtosecond laser ionization; fragmentation pattern; spectral phase.

Dedicated to: Eckart Rühl on the occasion of his 60th birthday.

1 Introduction

Chemical identification of organic molecules has been based on the analysis of fragmentation patterns observed in electron impact mass spectrometry (EI-MS) for many decades [1, 2]. The power of the approach originates from a combination of robust techniques with the advantages of chemically characteristic fragmentation channels. The robustness is connected to the fact that for most organic molecules the total cross section for ionization by electron impact (EI) exhibits a maximum around 70 eV and indeed the fragmentation pattern does not exhibit pronounced dependency on the electron energy. The simplicity of the approach

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turns into a disadvantage when the fragmentation pattern is not intrinsically characteristic of the species of interest. Such a situation applies in the attempt to distinguish structural isomers by EI-MS. A prototypical example here are the xylenes, *ortho*-xylene, *meta*-xylene and *para*-xylene, for which the EI-MS are virtually indistinguishable [3–5]. From the view point of chemical analysis there are in general alternative options for solving the problem, e.g. combination of a separation process and mass spectrometric examination. Numerous approaches have been reported to this end. We briefly discuss a few examples for isomer identification by means of a multi-stage technique. One common method is the coupling of gas chromatography (GC) with plain MS [6], as well as with tandem mass spectrometry (MSⁿ) [7]. Electrospray ionization combined with tandem mass spectrometry was used to distinguish chalcone isomers [8]. Mass spectrometry can also be combined with either plain liquid chromatography (LC) [9] or with high pressure liquid chromatography (HPLC) [10, 11] to distinguish between isomers. The variety of combinations between chromatographic techniques and mass spectrometry is enormous. However, all these methods are both time consuming and extensive, e.g. regarding the identification of the appropriate column in the chromatographic step. This leaves the quest for the distinction of isomers circumventing the need for chromatographic steps.

Coupling of mass spectrometry with optical selection schemes poses an alternative. Far-infrared light sources allow the tagging of isomer-specific molecular vibrations. Subsequent ionization of these tagged isomers with either multiphoton ionization in the UV or single photon ionization in the VUV constitutes the class of ion-dip spectroscopies [12], which can, indeed, be used for isomer-specific identification of chemical species [13]. Combination of IR excitation with light from an FEL with resonant MPI in the UV allowed distinguishing *ortho*-, *meta*- and *para*-isomers of aminophenol [14]. In the case of the *meta*-isomer even *cis* and *trans* conformers were assigned. Double resonance ion dip spectroscopy is particularly helpful in identifying structure-function correlation in peptide and protein systems [15].

Another efficient tool for identifying structural isomers or conformers is broadband rotational spectroscopy [16]. Schnell et al. demonstrated the distinction of 1,8-cineole and 1,4-cineole by means of broadband rotational spectroscopy using a chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer [17].

Vibrational spectroscopy in the far-infrared is also suited to distinguish between isomers. Different isomers of gold clusters, e.g. the Au₄ tetramer, have been observed in the range of 46–222 cm⁻¹. Assignment of the isomers, here, in general requires additional input from quantum chemical calculations [18].

Isomers can also be distinguished by their reactivity. The three xylene isomers mentioned above have been identified via their different reactivity towards V⁺

and VO^+ in a Fourier-transform ion cyclotron resonance mass spectrometer [19]. Still another approach for isomer identification is provided by Infrared photo-dissociation spectroscopy combined with suitable tagging of the ionized isomer by, e.g. argon [20]. This, however, requires a prior ionization of the sample.

The list of approaches for isomer specific analysis presented above is by no means complete. Yet all available approaches involve a considerable complexity. All optical techniques discussed above involve two different steps, one for ionization and one for dissociation or tagging. At this point we wish to draw the attention to fs-laser ionization mass spectrometry (fs-LIMS) [21, 22], a technique which can easily combine ionization and fragmentation in the interaction of a sample with a single laser pulse [23]. Fs-LIMS combines advantages of mass spectrometry and photoionization. First, as the approach utilizes a pulsed light source this enables us to employ time-of-flight mass spectrometry (ToF-MS), which provides high sensitivity and high mass resolution. Second, as femtosecond laser pulses are spectrally broad, this opens the possibility to use the spectral phase of the laser pulses as an additional parameter turning the approach into a multi-dimensional spectroscopy. This latter aspect does not have an analogue in EI-MS.

By now there is a considerable number of published reports on the distinction of structural isomers by shaped fs-laser ionization [24–26]. Different approaches of pulse shaping have been applied, some are based on the concept of systematically varying specific terms of the spectral phase, e.g. linear chirp [27] and binary pulse shaping [28]. Some others are based on optimizing experimental observables by means of a genetic algorithm [29]. For the xylenes, it has been demonstrated that the *ortho*- and the *para*-isomer can be distinguished in fs-LIMS either by binary phase pulse shaping [24, 25] or by simply imprinting a linear chirp of about -1000 fs^2 [26] onto fs-pulses at 800 nm wavelength. Zhu et al. [30] have demonstrated that *ortho*-, *meta*- and *para*-methyl-acetophenone can be distinguished via characteristic time constants for fragmentation in a chirped fs-laser field. Chirped fs-laser ionization has also been employed to a variety of topics in molecular physics including, e.g. the selective rotational excitation [31], and the control of dissociative ionization [32].

The relevant property for quantification of chirping is the spectral phase of the laser field with the linear chirp parameter α and the quadratic chirp parameter β as defined in the experimental section. Inherently, the characteristics of ionization processes depend on the spectral phase. For many highly non-linear ionization processes the ionization efficiency will decrease with increasing linear chirp parameter α . For ionization efficiencies scaling with the laser intensity I_{laser}^n , where n is a parameter reflecting the non-linearity of the excitation, this effect will be independent of the sign of the chirp. We refer to this situation as intensity-dependent chirp effect [33]. Recently, another distinctively

Scheme 1: Illustration of the structural isomers of difluorobenzene and benzenediamine.

different chirp effect has been observed. For several hydrocarbon molecules the ionization efficiency is not maximum for a transform limited laser pulse, but for negatively linear chirped laser fields with $\alpha(Y_{\max})$ on the order of -1000 fs^2 [33, 34]. In this situation for a given absolute value of α the ion yield Y for $-\alpha$ can be several orders of magnitude larger than for $+\alpha$. This is referred to as sign-dependent chirp effect. Evidently, in these experiments the sequence of frequency components in the laser spectrum can enhance or suppress the ionization efficiency. Sign of the chirp effects cannot only be observed for the formation of parent ions but also in fragmentation processes [35, 36]. In general, intensity-dependent chirp effects and sign-dependent chirp effects will concur. In recent work the authors group also demonstrated the possibility to control fragmentation processes in ethane by chirping fs-laser pulses. We note that this control can be established by either systematically varying the linear or quadratic chirp parameter or by applying a genetic algorithm to a 612 pixel representation of the spectral phase [37].

In the current work we present a systematic investigation of the variation of the spectral phase in fs-LIMS for two different *ortho*-, *meta*- and *para*-disubstituted benzenes, i.e. difluorobenzene (DFB) and benzenediamine (BDA). Structures of these disubstituted benzene isomers are illustrated in Scheme 1.

We will demonstrate that we are able to distinguish the three structural isomers for DFB as well as BDA by applying suitable linear (and quadratic) chirp concepts. To this end total mass-resolved ion yields, Y , as well as ion yield ratios will be analyzed, demonstrating isomer-specific enhancement or suppression. Particular attention will be given to the competition between intensity-driven and non-intensity-driven fragmentation channels. In case of the difluorobenzene isomers the mechanism for the formation of specific fragments and the relevance of a ring opening as start of the fragmentation process will be discussed, as it is known for difluorobenzene [38].

2 Experimental

Experiments aimed at distinguishing structural isomers by chirped fs-LIMS have been conducted in a vacuum chamber housing a home-built time-of-flight mass spectrometer (ToF-MS) [32]. The ToF-MS is of the Wiley-McLaren type. Typical electric field strength in the ionization region are 880 V/cm. The mass resolution is on the order of 300:1 – sufficient for the scientific questions tackled in this work. Commercial Reflectron ToF-MS can reach a mass resolution of several times 10,000:1. The samples are introduced into the experimental chamber as an effusive beam. Typical pressures were set to the range between $7 \cdot 10^{-7}$ mbar and $4 \cdot 10^{-6}$ mbar during data acquisition.

The femtosecond laser system consists of a femtosecond oscillator (Synergy, Femtolasers) and a chirped pulse amplifier (Odin, Quantronix). The resulting laser pulses possess a central wavelength of 807 nm and a spectral width (FWHM) of about 35 nm. The spectral phase is varied by means of a folded 4f-shaper setup with a spatial light modulator (SLM640, Jenoptik) in the Fourier plane. The resulting laser pulses are characterized with a Grenouille (8–50, Swamp Optics) and focused into the ionization region with a concave mirror ($f = 7.5$ cm).

The approach of tailoring fs-laser pulses requires manipulation of the spectral phase, which can be expressed as a Taylor expansion of the form $\partial^n \phi / \partial \omega^n$:

$$\begin{aligned} \phi(\omega) = & \phi_0(\omega_0) + (\omega - \omega_0) \cdot \left. \frac{1}{1!} \frac{\partial \phi}{\partial \omega} \right|_{\omega=\omega_0} + (\omega - \omega_0)^2 \cdot \left. \frac{1}{2!} \frac{\partial^2 \phi}{\partial \omega^2} \right|_{\omega=\omega_0} \\ & + (\omega - \omega_0)^3 \cdot \left. \frac{1}{3!} \frac{\partial^3 \phi}{\partial \omega^3} \right|_{\omega=\omega_0} + \dots \end{aligned} \quad (1)$$

The most relevant component in the context of the current work is the second order spectral phase, whose coefficient is the linear chirp parameter α

$$\alpha = \frac{1}{2!} \cdot \frac{\partial^2 \phi(\omega)}{\partial \omega^2} \quad (2)$$

A linear chirp of the laser pulse can easily be generated by writing a parabolic second order spectral phase to a spatial light modulator (SLM) [39]. A quadratic chirp can be generated by writing a cubic third order spectral phase to the SLM.

Physically a linear chirp is equivalent to a linear variation of the instantaneous laser frequency with time. As demonstrated by Balling et al. [40] imprinting a linear chirp onto a transform-limited laser pulse with duration τ_0 will inevitably result in an increasing pulse duration τ_α as given by

$$\tau_{\alpha}^2 = \tau_0^2 + \left(\frac{8 \cdot \ln(2) \cdot \alpha}{\tau_0} \right)^2 \quad (3)$$

In general the spectrum and the pulse energy, E_p , are kept constant during chirping, therefore the pulse peak intensity decreases with increasing linear chirp parameter α . This effect is independent of the sign of α . A quadratic chirp is leading to a characteristic pulse train as, e.g. demonstrated in ref. [37].

There are some subtle differences between the optical path to the Grenouille on one hand, and to the vacuum chamber on the other leading to minor differences in the pulse duration. The largest of these effects is caused by the entrance window to the experimental chamber (3 mm thickness) leading to a broadening of 0.7 fs, which is still much smaller than all chirp effects discussed in this work. For a comparison we note that a linear chirp of +250 fs² corresponds to a broadening of the pulse from 45 fs (transform-limited pulse) to 54.5 fs. A sketch of the overall setup can be found in ref. [37].

3 Results

This section is organized as follows: We first present overall mass spectra for BDA and DFB. Subsequently the linear and quadratic chirp dependence of ion yields (Y) will be shown as well as particular ion yield ratios. The choice of these ion yield ratios will be explained also.

3.1 Overview Mass Spectra

Figure 1 shows mass spectra of the *ortho*-isomers of the BDA and the DFB employing transform-limited laser pulses. Both MS exhibit a rich fragmentation pattern. The base peak is in both cases the singly-charged parent ion M^+ , i.e. $m/z=108$ for BDA and $m/z=114$ for DFB. An intense signal is observed for half the mass-to-charge ratio of the parent ion, i.e. at $m/z=54$ for BDA and $m/z=57$ for DFB. At first glance, two assignments appear possible, (i) fragmentation of the parent molecule into two identical halves and (ii) the formation of a doubly-charged parent ion M^{2+} . The following findings support assigning these peaks to the doubly-charged parent ion. First, the break-up of the parent molecule into two identical halves would require the breaking of two carbon–carbon bonds. This is energetically unlikely and would be expected to lead to a considerable release of kinetic energy, which is, however, not observed, even under conditions of very

Fig. 1: fs-Laser ionization mass spectra of *o*-BDA (left, $E_p = 17 \mu\text{J}$, $p = 6 \cdot 10^{-7}$ mbar) and *o*-DFB (right, $E_p = 45 \mu\text{J}$, $p = 5.5 \cdot 10^{-6}$ mbar) obtained at 807 nm with Fourier-transform limited laser pulses.

low electric draw out fields in the ion source. This conclusion holds for two possible pathways, (i) $M^+ \rightarrow (M/2)^+ + M$ and (ii) $M^{++} \rightarrow (M/2)^+ + (M/2)^+$. Second, there are peaks observed at $m/z = 57.5$ and $m/z = 54.5$ with a relative intensity of about 6% compared to the peaks at 57 and 54, respectively. These peaks can only be assigned to the ^{13}C isotopomer of the respective doubly-charged parent ions.

Noteworthy, measuring the respective mass spectra for the remaining *m*- and *p*-isomers under the same experimental conditions for transform-limited laser pulses leads to data indistinguishable from the spectra shown in Figure 1. This stimulated attempts to distinguish structural isomers by tailoring the fs-laser pulses.

In the following discussion, we will direct particular attention to the ion yields of the singly-charged and the doubly-charged parent ion. For DFB $m/z = 94$ and $m/z = 88$ will also be discussed. The latter can be attributed to the elimination of a neutral HF molecule and a neutral acetylene molecule, respectively. Here, the corresponding ion yield ratios referenced to the singly-charged parent ion will be presented.

3.2 Benzenediamine

The chirp dependence of the singly-charged parent ion yield $Y(m/z = 108)$ and the doubly-charged parent ion yield $Y(m/z = 54)$ of *o*-BDA are shown in Figure 2 as a function of the linear chirp parameter α . Both ion yields are dominated by an intensity-dependent chirp effect as evidenced by the maximum being observed for the transform-limited laser pulses. However, subtle differences occur, e.g. in

Fig. 2: Linear chirp dependence of ion yields at the m/z indicated for *ortho*-BDA obtained at 807 nm, $E_p = 20.5 \mu\text{J}$, $p = 6 \cdot 10^{-7}$ mbar. The data are normalized to the maximum yield of the singly-charged parent ion. Error bars are included but mostly hidden by the data points.

the regime of negative linear chirp the yield $Y(m/z = 108)$ decreases steeper than $Y(m/z = 54)$.

The subtle differences mentioned above ultimately open access to distinguishing the structural isomers. This becomes evident when plotting ion yield ratios rather than absolute ion yields. To this end, Figure 3 shows the ion yield ratios $Y(m/z = 54)/Y(m/z = 108)$ as function of the linear (left) and of the quadratic (right) chirp parameter for all three isomers, the *o*-, *m*- and *p*-isomer.

Fig. 3: Ion yield ratios of doubly-charged parent ion referenced to the singly-charged parent ion of BDA isomers as function of the linear (left, $E_p = 20\text{--}23 \mu\text{J}$, $p = 6\text{--}8 \cdot 10^{-7}$ mbar) and quadratic (right, $E_p = 18\text{--}22 \mu\text{J}$, $p = 6\text{--}8 \cdot 10^{-7}$ mbar) chirp parameter. Error bars are included but in part smaller than the data points.

The overall trend for the variation of the ion yields shown in Figure 3 is similar, exhibiting a pronounced sign dependent chirp effect. For all three isomers the maximum for the yield ratios $Y(m/z=54)/Y(m/z=108)$ is observed around $\alpha \approx -1000 \text{ fs}^2$. Note, that the absolute ion yields for $Y(m/z=54)$ and $Y(m/z=108)$ were dominated by intensity-driven chirp effects. The pivotal observation is, that the absolute ion yield ratio $Y(m/z=54)/Y(m/z=108)$ is distinctly different for the three isomers, the values being largest for the *p*-isomer and smallest for the *o*-isomer for the entire range of chirp parameters investigated. This observation constituting the distinction of the isomers, will be rationalized in the discussion section.

3.3 Difluorobenzene

As a second example for di-substituted benzene derivatives, we have investigated the *o*-, *m*- and *p*-isomers of di-fluorobenzene. The absolute ion yields for the singly- and the doubly-charged parent ion is provided as Supplementary Material. Similar to the observation in the DBA system the ion yield characteristic is intensity driven and does not allow for a distinction of the isomers. In order to investigate, whether the ratio of the doubly-charged parent ion yield referenced to the singly-charged parent ion is a suitable observable for distinguishing between the isomers of DFB this ratio, $Y(m/z=57)/Y(m/z=114)$, is depicted in Figure 4.

Evidently, the data nearly fall on top of each other. There is only one regime, i.e. around $\alpha \approx +10,000 \text{ fs}^2$, where the ion yield ratio $Y(m/z=57)/Y(m/z=114)$

Fig. 4: Ion yield ratios of doubly-charged parent ion compared to the singly-charged parent ion of DFB isomers as function of the linear (left, $E_p = 40 \mu$, $p = 9 \cdot 10^{-6} \text{ mbar}$) and quadratic (right, $E_p = 18\text{--}22 \mu$, $p = 6\text{--}8 \cdot 10^{-7} \text{ mbar}$) chirp parameter. Included error bars are hidden in part by the data points.

shown is larger for the *p*-isomer compared to the other two isomers. Therefore, the distinction of the three isomers is not possible on this basis of data.

However, we have identified other ion yield ratios which allow to distinguish the structural isomers of DFB. There are two characteristic fragmentation channels in DFB, (i) the loss of a neutral HF molecule leading to a charged fragment at $m/z=94$

and (ii) the loss of neutral acetylene leading to a charged fragment at $m/z=88$

We have investigated the yields for both fragmentation channels as a function of the linear chirp parameter α . In Figure 5, the respective ion yield ratios referenced to the parent ion yield are depicted. At first glance, we note that the all data traces exhibit sign-dependent chirp effects. None of the channels appears to be intensity driven. For the acetylene loss, the ion yield ratios for the different isomers cross each other while for the HF loss there is a clear order of the ion yield ratios for the three isomers.

Upon closer inspection, we note that the overall variation of the ion yields discussed with α is largest for the *o*- and the *p*-isomer. The variation is small for the *m*-isomer. For both reaction channels, the largest value for an ion yield ratio is observed for the *p*-isomer and for $>10,000 \text{ fs}^2$. For the acetylene loss channel, $Y(m/z=88)/Y(m/z=114)$ exhibits a local minimum around $\alpha \approx 0 \text{ fs}^2$ for the *o*- and the *p*-isomer. For negative linear chirp parameters, the ion yield ratio decreases in the order *o*-, *p*-, *m*-isomer. For positive linear chirp parameters the corresponding

Fig. 5: Linear chirp dependencies for the ion yields corresponding to the elimination of acetylene (left, $E_p = 40 \mu\text{J}$, $p = 8 \cdot 10^{-6} \text{ mbar}$) and neutral HF (right, $E_p = 40 \mu\text{J}$, $p = 8 \cdot 10^{-6} \text{ mbar}$) referenced to the singly-charged parent ion yield. Error bars are included, but in part hidden by the data points.

order is *p*-, *o*-, *m*-isomer. In fact, the ion yield ratio $Y(m/z=88)/Y(m/z=114)$ is larger for the *o*- than the *m*-isomer for all values of α investigated. Apparently, it is the *p*-isomer, which makes the quantitative distinction difficult. The striking difference in the HF-loss data is that there the order of the ion yields ratios is almost independent of α . Only for pronounced negative linear chirp, the ion yield ratios are similar within the error limits for the *m*- and the *p*-isomer. This appears to be advantageous for distinguishing the isomers. An attempt for rationalizing these findings will be presented in the following section.

4 Discussion

In the result section, we have presented various ion yield ratios exhibiting in part characteristic signatures of the respective three isomers. The observations stimulate two questions: (i) which static molecular properties favor the distinguishability of the three isomers? and (ii) which dynamical properties favor the distinguishability?

In the case of the BDA the distinguishability of the three isomers appears to correlate with the ionization energies of the three isomers. Most of the literature reports agree that for BDA the ionization energies decrease in the order *o*-BDA > *m*-BDA > *p*-BDA as listed in Table 1.

Although to the best of our knowledge no published reports are available on the second ionization energies, it appears plausible that they may follow the same order as the first ionization energies.

Seemingly, there is a correlation between order of the ionization energies in the BDA isomers and order of the ion yield ratios between double ionization and single ionization $Y(m/z=54)/Y(m/z=108)$. Additional double ionization experiments would be required to confirm this hypothesis. Double ionization energies are accessible by either photon or electron impact studies [43]. Such experiments are not available to our group.

For comparison, the first ionization energies of the DFB isomers are also listed in Table 1. In accordance with the BDA findings one would expect the highest ion

Tab. 1: First ionization energies of the different structural isomers.

Isomer	BDA [41] /eV	DFB [42] /eV
<i>Ortho</i>	7.69	9.30
<i>Meta</i>	7.60	9.34
<i>Para</i>	7.34	9.16

Fig. 6: Illustration of the number of statistical possibilities for HF elimination from *o*-, *m*- and *p*-isomers of DFB.

yield ratio for the *para*-isomer. This is indeed observed for large positive values of the linear chirp parameter (cf. Figure 4). However, the relative importance of double ionization appears to change as a function of α in the DFB-isomers and a quantitative distinction by means of the ion yield ratio $Y(m/z=57)/Y(m/z=114)$ is difficult. Overall the relative energetic differences in the ionization energies are smaller in the DFB isomers ($\approx 2\%$) compared to the BDA isomers ($\approx 4.6\%$), favoring the distinction in the latter case.

We demonstrated that the ion yield ratios regarding elimination of neutral HF and acetylene exhibit large differences in the linear chirp dependence of the isomers. In the case of the HF-elimination a rationalization appears plausible on statistical grounds. As depicted in Figure 6 there are only two hydrogen atoms next to a fluorine atom in the *o*-DFB. There are three hydrogen atoms neighboring fluorine atoms in *m*-DFB and four hydrogen atoms neighboring fluorine atoms in *p*-DFB. Consequently the statistical weight of the respective HF-elimination should vary as 2:3:4. The same qualitative order is observed experimentally.

One may attempt to apply a similar statistical argument for the acetylene loss channel. Acetylene loss requires ring opening. The positions of possible ring opening and consequently the statistical weight for acetylene loss from the different isomers can be worked out [44]. However, it turns out that the agreement with experimental observation is poor. Evidently, the dynamics of this reaction channel does not favor statistical characteristics. Instead the very different chirp dependencies in the acetylene loss channel can partly be attributed to differences in the time-dependent population evolution for the three structural DFB-isomers when excited to the cationic $\tilde{A}$ or $\tilde{D}$ state [45].

The current work demonstrates that chirped fs-LIMS is a potentially attractive tool for distinguishing structural isomers of molecules. This conclusion is further supported by previous work from our group [26], as well as by extensive work from the Dantus group [24, 25]. While the authors group in general pursue systematic linear (or quadratic) chirp concepts, the Dantus group in general

adopt binary pulse shaping for the distinction of structural isomers. The systematic chirp may be regarded having the advantage to enable interpretation of the effects observed.

From the viewpoint of chemical analysis the conclusion presented above implies that any of the isomers can be uniquely identified – provided that the sample is chemically pure. Ultimately, the goal of this research is to enable a quantitative analysis of a mixture of structural isomers. This is still a challenge for conventional sample introduction as employed in the current work. In fact, we have carried out a number of experiments premixing structural isomers of the title molecules in a specific ratio. In the course of these experiments, we realized that differences in the vapor pressure of the individual isomers in a mixture introduces a considerable complication of the analysis. For the BDA, e.g. at 298 K a vapor pressure of 0.202 Pa is obtained for the *ortho*-isomer, 0.065 Pa and 0.0205 Pa is observed for the *meta*- and *para*-isomer, respectively [1]. We propose to overcome this difficulty by constructing a sample introduction independent of the vapor pressure of the analytes, e.g. a spray-like introduction of the sample to the source of the ionization spectrometer.

Fs-LIMS is a viable approach for chemical analysis. However, there is still a long way to go, before turning it into a routine technique. We hope that the current work stimulates further efforts along this goal. Ultimately, the reward would be a technique, which makes separation steps obsolete.

5 Summary

The distinction of the structural isomers of two disubstituted benzene species, i.e. benzenediamine and difluorobenzene has been investigated by chirped femto-second laser ionization mass spectrometry. We demonstrate the ability to clearly distinguish *ortho*-, *meta*- and *para*-isomers of BDA and DFB by means of specific ion yield ratios. Although there seems to be no universal characteristics of disubstituted benzenes in chirped laser fields, we have been able to rationalize our findings. In case of BDA isomers the linear and quadratic chirp dependencies of the ion yield ratios of doubly-charged parent ion relative to the singly-charged parent ion enable the distinction. The order of the ion yield ratio reflects the order in the first ionization energies and gives evidence for a possible sequential double-ionization process. For the distinction of the DFB isomers the ion yield ratios corresponding to the HF elimination channel and acetylene loss channel are suitable. Here, we have to consider statistical fragmentation as evidenced in the HF loss [$Y(m/z=94)/Y(m/z=114)$] but also competition of statistical and dynamic processes as operative in the acetylene loss [$Y(m/z=88)/Y(m/z=114)$].

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