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Distinction of *ortho*- and *para*-Xylene by Femtosecond-Laser Mass Spectrometry

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The distinction of structural isomers is one of the key tasks in analytical chemistry. In the case where classical electron impact mass spectrometry leads to indistinguishable mass spectra, combined techniques as gas chromatography/mass spectrometry (GC/MS) and so forth can be employed. However, the demand for fast online techniques which circumvent the need for separation is still eminent. One obvious alternative is based on photoionization (PI), in particular PI by laser radiation. Besides from laser mass spectrometry operating in the frequency domain,[1] femtosecond-laser mass spectrometry (fs MS) has been implemented as a tool for molecular identification.[2–8] Recently, it was suggested that fs-pulse shaping may even provide zero false positives in mass spectrometry.[9] A prototypical system of isomers are the xylenes. Here, the distinction of *o*-xylene and *p*-xylene may serve as a benchmark test.

There are now several well established concepts for fs-pulse shaping. Binary phase shaping of pulses has been systematically employed as a compact and easily accessible technique[10,11] for coherent control schemes.[12] However, binary phase shaping may produce complex pulse shapes. Understanding the underlying control mechanisms for such pulses is not straight forward, and the distinction between trivial and nontrivial control aspects becomes difficult.[13] In contrast to that, linear chirping of fs-laser pulses leads to rather simple pulse shapes, in particular a linear time dependence of the laser frequency within the pulse.

Herein, we describe laser ionization mass spectrometry of *o*-xylene and *p*-xylene employing linearly chirped fs-laser pulses. The results will be discussed in comparison to the work of Dela Cruz et al.[4] who reported mass spectra of the same isomers utilizing binary phase pulse shaping. While Dela Cruz et al. concentrated on the ratio of the $C_7H_7^+$ ion yield to the parent ion yield, we will demonstrate the additional advantage of investigating small fragments such as C^+ and CH_3^+.

Experimental Section

The dissociative ionization of *o*- and *p*-xylene isomers has been investigated in a home-made linear time-of-flight mass spectrometer (TOF MS). The TOF MS consists of a double-stage acceleration and a 30 cm field-free drift tube combined with a tandem microchannel plate detector. Very high collection efficiency is ensured by operating the ion source at a field of 300 V cm^{-1}, preventing at the same time discrimination of ions. The ionizing radiation is generated in a fs-laser system consisting of a 20 fs Ti:Sapphire oscillator (Femtosource Compact, Femtolasers Inc.) seeding a multipass amplifier (Odin, Quantronix Inc.). The amplifier delivers laser pulses at a center wavelength of 805 nm with a repetition rate of 1 kHz. The full bandwidth of the spectrum is approximately 40 nm.

The pulses were characterized using the frequency-resolved optical-gating (FROG) technique (GRENOUILLE, Swamp Optics). Pulse shaping is realized with a spatial-light modulator (SLM) with a liquid-crystal unit consisting of 640 pixels (SLM-S640, Jenoptik). Measured phase distortions were corrected with the pulse shaper in order to obtain approximately transform-limited (TL) pulses with a typical pulse duration τ_0 of 40 fs. Linear chirp was introduced using the pulse shaper by introducing quadratic phase versus frequency. This did not affect the pulse energy. By Equation (1)[14] the resulting pulse duration τ was directly correlated to the applied linear chirp parameter $\alpha = 1/2 * \partial^2\phi/\partial\omega^2$ measured in fs^2, where $\phi(\omega)$ is the spectral phase and ω is the angular frequency.

$$\tau^2 = \tau_o^2 + (8 \cdot \alpha \cdot \ln 2/\tau_0)^2 \qquad (1)$$

Positive (up chirp) and negative (down chirp) values of α correspond to an increasing or decreasing frequency with time, respectively.

The predominance of linear chirp has been confirmed by FROG measurements. The sign of the chirp was calibrated by introducing optical material of known group velocity dispersion into the beam path.

The laser radiation was focused by an $f = 75$ mm aluminum mirror. The experiments shown in this work have been obtained at laser-pulse energies in the range of 5 to 100 μJ per pulse. Assuming classical optics for the airy disc we estimate a maximum intensity for the case of TL pulses of $2 \cdot 10^{13}$ W cm^{-2}. The laser light was linearly polarized, with the polarization plane parallel to the spectrometer axis.

TOF spectra were recorded by typically averaging over 5000 laser shots. The sample has been introduced into the vacuum chamber under thermal conditions. The background pressure of the vacuum chamber was better than $2 \cdot 10^{-7}$ mbar. The operating pressure was typically $6 \cdot 10^{-7}$ mbar. *O*-xylene and *p*-xylene have been purchased from Acros and J. T. Baker, respectively. Purity was in both cases specified as better than 99%. The samples have been used without further purification.

Results

The dissociative ionization of *o*- and *p*-xylene isomers has been investigated employing fs-laser pulses with a center wavelength of 805 nm as a function of laser-pulse energy and linear chirp, respectively. Pulse energies were between 10 and 100 μJ per pulse, that is, slightly below those pulse energies typically used in investigations by the Dantus group.[4,8] This may be considered a regime of moderate intense laser fields.[15] Typical TOF spectra of the *o*- and *p*-xylene isomers measured with unchirped pulses at pulse energies of 21 μJ and 80 μJ, respectively, are shown in Figure 1. A rich fragmentation pattern is ob-

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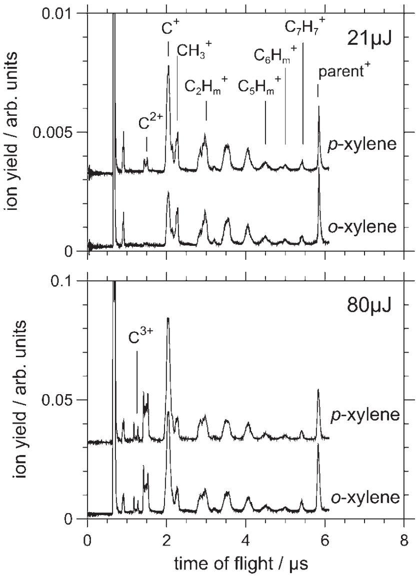

Figure 1. TOF spectra of *o*- and *p*-xylene isomers measured with unchirped pulsed. The pulse energy was 21 μJ and 80 μJ, respectively. The spectra are shifted vertically for clarity. The C^{2+} and C^{3+} ion signals exhibit a double peak structure corresponding to the ions with initial velocity towards and away from the detector.

served. The parent ion and the largest fragment, the $C_7H_7^+$ ion, are clearly discernible as are very small fragments, for example, the C^+ and the CH_3^+. The latter ions turn out to carry particular information on the structure of the parent isomer. Intermediate size fragments of the type $C_2H_m^+$ to $C_6H_m^+$, where *m* indicates the number of H atoms, are not fully resolved.

Ionization and fragmentation of the molecules is induced in a single laser pulse. Clearly, the parent-ion signal (mass = 106 u) is observable for all pulse energies investigated. However, already for a pulse energy of 21 μJ the parent-ion yield is smaller than the yield of some of the fragment ions. The observed fragments and their yield depend on the laser-pulse energy. For example, the C^{3+} ion is not observed for a laser-pulse energy of 21 μJ, whereas it is present at 80 μJ (Figure 1).

For the C^+ ion and the C^{2+} ion pronounced differences of the ion yield of the isomers are observed at a pulse energy of 21 μJ (Figure 1). The ratio of CH_3^+ to C^+ ion yields is significantly larger for *p*-xylene compared to *o*-xylene. Furthermore, the C^{2+} ion yield is significantly larger in *p*-xylene compared to *o*-xylene. These differences already indicate the feasibility of distinguishing the two isomers of xylene on the basis of their fs-laser mass spectra. Smaller differences occurring for the ion yield of other fragment ions will not be discussed here. With increasing pulse energy the pronounced differences decrease. At a pulse energy of 80 μJ they have nearly vanished (Figure 1).

In the following we discuss the chirp dependence of ion yields. For the parent and the $C_7H_7^+$ ions the maximum ion yield is observed for the TL pulse where $\alpha = 0$. With increasing linear chirp the ion yields decrease. The decrease is basically symmetric with respect to the TL pulse, that is, it is independent of the sign of the chirp. The chirp dependence of the ion yields can be approximately described by a Lorentzian function. Since the pulse energy is not changed upon chirping, but the pulse duration increases concomitantly, this chirp dependence reflects an intensity effect. Nevertheless the chirp dependence of specific ion yields contains characteristics of the parent isomers. For both isomers the chirp dependence of the parent-ion yield follows a broader Lorentzian function than that for the $C_7H_7^+$ ion (Figure 2). Furthermore, the Lorentzian describing the parent ion of *o*-xylene has a larger width than that for *p*-xylene, and the Lorentzian for the $C_7H_7^+$ ion formed from *o*-xylene has a slightly larger width than that from *p*-xylene.

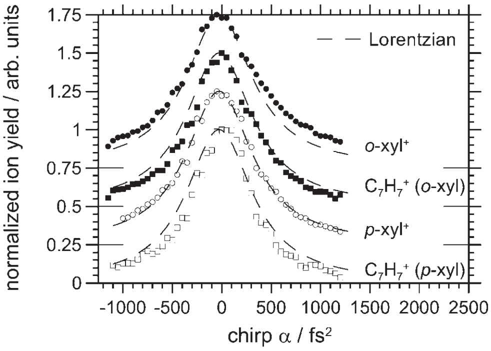

Figure 2. Normalized ion yield of the parent ion and the $C_7H_7^+$ ion for *p*- and *o*-xylene for varying linear chirp. The pulse energy was 21 μJ. To guide the eye the same Lorentzian lineshape function (full width at half maximum, FWHM = 810 fs^2) is overlayed over all experimental data sets. The yields are shifted vertically for clarity.

In addition to looking at the absolute ion yields, it is also helpful to discuss ratios of ion yields. As an example Figure 3 shows the ratio of $C_7H_7^+$ ion yield to parent-ion yield for the two isomers as a function of chirp. Evidently the width of the data trace is significantly larger for *o*-xylene compared to *p*-xylene. We conclude that the distinction of *o*-xylene and *p*-xylene is possible on the basis of the chirp dependence of appropriate ion yields. In this case the distinction is based on the formation of the $C_7H_7^+$ ion as was the case in the work of Dela Cruz et al. employing pulses with binary phase modulation.[4]

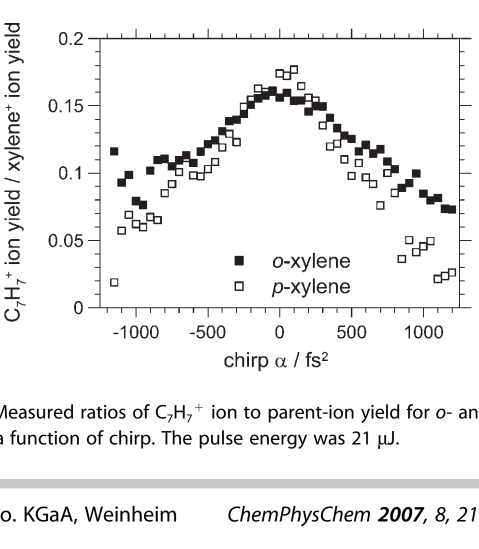

Figure 3. Measured ratios of $C_7H_7^+$ ion to parent-ion yield for *o*- and *p*-xylene as a function of chirp. The pulse energy was 21 μJ.

For the parent ion and the $C_7H_7^+$ ion changing the sign of chirp led only to minor differences in the measured ion yields for both of the xylene isomers. For some of the smaller fragment ions we clearly observe an influence of the sign of the chirp, in particular for the *o*-xylene isomer (Figure 4). The ratio of the CH_3^+ ion yield to C^+ ion yield as a function of the linear chirp is strongly asymmetric with respect to zero chirp for laser pulse energies of 26 μJ and below. More specifically for negative chirp the formation of the CH_3^+ ion is favored compared to the C^+ ion. This is in line with the general trend that negative chirp tends to favor that reaction channel with the energetical lower dissociation limit.[16] Furthermore, the absolute value of the ratio of the CH_3^+ ion yield to C^+ ion yield is remarkably higher for *o*-xylene than for *p*-xylene at pulse energies of 26 μJ and below. This difference vanishes for higher pulse energies (c.f. Figure 1).

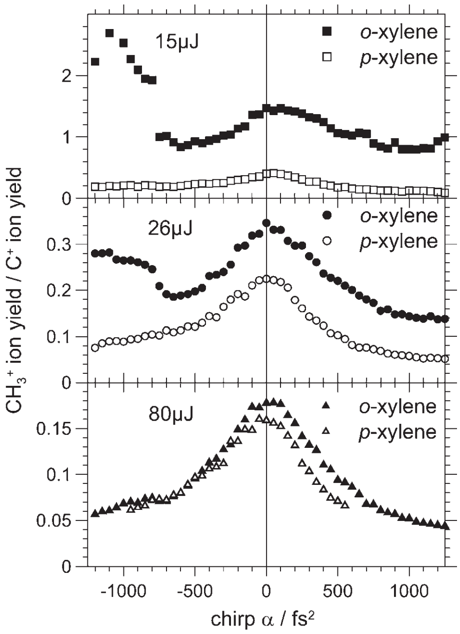

Figure 4. Measured ratios of CH_3^+ ion and C^+ ion yield of *o*- and *p*-xylene as a function of chirp. The pulse energy was 15 μJ, 26 μJ, and 80 μJ, respectively.

The influence of the sign of the chirp is even more pronounced for the yield of doubly charged carbon atoms, C^{2+}. At a laser-pulse energy of 26 μJ the ratio of C^{2+} ion yield to parent-ion yield is nearly zero for *o*-xylene for negative chirp, but distinctly different from zero for *p*-xylene (see Figure 5). This directly opens the possibility of quantitative analysis of isomer mixtures, since the relative yield of C^{2+} ions for chirp $\alpha \approx -1000$ fs^2 directly correlates with the amount of *p*-xylene in the mixture. Such an experiment is currently underway in our laboratory. For pulse energies even lower than 26 μJ the yield of C^{2+} ions is too small to be measured accurately.

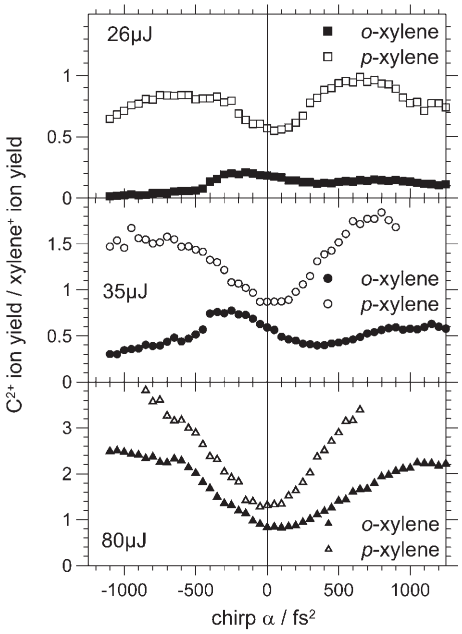

Figure 5. Measured ratios of C^{2+} ion and parent-ion yield of *o*- and *p*-xylene as a function of chirp. The pulse energy was 26 μJ, 35 μJ, and 80 μJ, respectively.

Discussion and Summary

What is the origin of the ability to distinguish isomers by fs-laser ionization? In conventional electron impact mass spectrometry the excitation energy, typically 70 eV, is transferred in a vertical transition. Chemical fragmentation only takes place after the excitation. Fs-laser ionization on the other hand is a highly nonlinear process. When operated around 805 nm as in the current work formation of small fragment ions involves several tens of photons. While TL pulses are so short that again fragmentation can only take place after the end of the laser pulse, this does not hold for the strongly chirped laser pulses. For example, the chirp parameter $\alpha \approx -1000$ fs^2 corresponds to a pulse duration of $\tau \approx 144$ fs. It appears possible that geometry relaxation occurs during the laser pulse ultimately enabling the distinction of isomers. Here it is particularly interesting to note, that the atomic fragments C^+ and C^{2+} carry the memory of the structural identity of their parent molecules. It seems conceivable that structure related information can also be obtained from Coulomb explosion in intense laser fields.[17–20]

We have demonstrated that the distinction of structural isomers is possible by means of fs-laser mass spectrometry employing linearly chirped laser pulses. Two different situations are relevant. For some ion signals the distinction of the isomers is possible based on intensity effects. These are by and in large associated with a chirp dependence which is symmetric with respect to the TL pulse. This situation applies for the parent ion and for the largest fragment $C_7H_7^+$. The results observed are fully compatible with reports from Dantus and coworkers.[4] For the smaller fragments, which has not been investigated in detail before, the distinction of the isomers is demonstrated to be possible based on a chirp effect which depends on the sign of the chirp. For the future it appears rewarding to further develop the concepts presented here to an analytical tool for trace analysis.

The largest fragment ion formed in the fragmentation of xylenes, the $C_7H_7^+$ ion, is the subject of considerable interest itself.[21] There are three important isomers, 1) the benzylium, 2) the tropylium and 3) the tolylium. It is not a priori clear, which of these isomers dominates in the fs-mass spectra. At this point we can only speculate, that the distinction of xylene isomers may be affected by the different mechanisms leading to the formation of either fragment isomer.

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