

Resonance Enhanced Laser Mass Spectrometry of Potential Dioxin Surrogates: REMPI spectra of the Mono-, Di- and Trichlorophenols

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Abstract:

The one-color two-photon REMPI (*resonance-enhanced multiphoton ionization*) spectra of several chlorinated phenols have been recorded. In detail the spectra of *o*-, *m*- and *p*-chlorophenol as well as of 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dichlorophenol and 2,4,5-trichlorophenol are presented. Chlorinated phenols are potential surrogates for dioxins in the flue gas of e.g. waste incinerators.

Introduction

Resonance-enhanced multiphoton ionization time-of-flight mass spectrometry (REMPI-TOFMS) is an analytical technique for selective detection and real-time monitoring of trace compounds in complex gas mixtures. In particular, applications of REMPI-TOFMS for on-line trace analysis of flue gases emitted from different incinerators have been reported^{1,2}. This includes the monitoring of monochlorobenzene, which is a PCDD/F-surrogate, from waste incineration plant flue gases. However, the REMPI-TOFMS technique most likely is not applicable for on-line real-time monitoring of higher chlorinated polychlorinated dibenzo-*p*-dioxins/furans (PCDD/F) because of their low concentration and their low ionization efficiency due to molecular physical reasons.

It has been reported that in addition to the chlorobenzenes also the chlorophenols, which are known as precursors in several PCDD/F formation processes, have a close relationships to the concentration of PCDD/F and the International Toxicity Equivalent (I-TEQ)³. A few Jet-REMPI spectra of chlorophenols have been presented up to now^{4,5}. In this study, we measured the REMPI spectra of all mono-, di- and trichlorophenols with the effusive molecular beam inlet technique.

Experimental

Fundamentals of the REMPI-TOFMS technique have been described in detail elsewhere⁶. The experiments have been carried out at the GSF research center in Germany. The experimental setup consists of a linear time-of-flight mass spectrometer with an effusive capillary inlet system². The effusive capillary inlet allows no adiabatic cooling of the samples but is very robust and rugged and thus applicable for field applications^{1,2}. The samples were seeded in air. Tunable laser radiation was generated either by a frequency-doubled excimer-laser-pumped dye laser (Lambda Physik, FL 2002 and LPX 100, Germany) or by a frequency-doubled, Nd:YAG-laser pumped narrow-band optical parametric oscillator (Spectra Physics, Quanta-Ray MOPO-HF and Pro 270, USA). The laser pulses are crossing the effusive molecular beam in the center of the TOFMS ion source. Induced ions are accelerated by a repulsive potential into a flight tube and were detected by an assembly of microchannel plates. The mass selected REMPI spectra were acquired by registering the area of the respective molecular ion peak in the TOF mass spectrum as a function of the laser wavelength. A boxcar integration system (SR 250 Stanford Research System, USA) was used for this purpose. The data is digitized by a triggered A/D computer interface (SR245 Stanford Research System, USA) and transferred via a GPIB interface to a personal computer system. Home written software (based on LabView, National Instruments, USA) was used for data recording, laser control and data analysis. The spectra were normalized with respect to the square of the laser power (with exception of Fig 1d). REMPI mass spectra were recorded with a digital storage oscilloscope (LeCroy, Type 9361, Switzerland).

Results and Discussion

Figure 1 shows the effusive molecular beam REMPI spectra of the origin region of the first singlet transition (S_1) of the monochlorophenols. All of them are measurable with excellent efficiency. Previously a Jet-REMPI study on these compounds has been reported by Tembreull et al.⁴. The spectrum of *o*-chlorophenol shows efficient ionization at its origin region (278-279 nm), although a two-photon ionization process is not possible (the two-photon ionization limit is 267.25 nm⁴). Figure 1d shows the REMPI spectrum of *m*-chlorophenol in a wider wavelengths range. The excitation $S_1 \leftarrow S_0$ is measured around 270 nm, but no further transition ($S_2 \leftarrow S_0$) was observable at shorter wavelengths down to 220 nm.

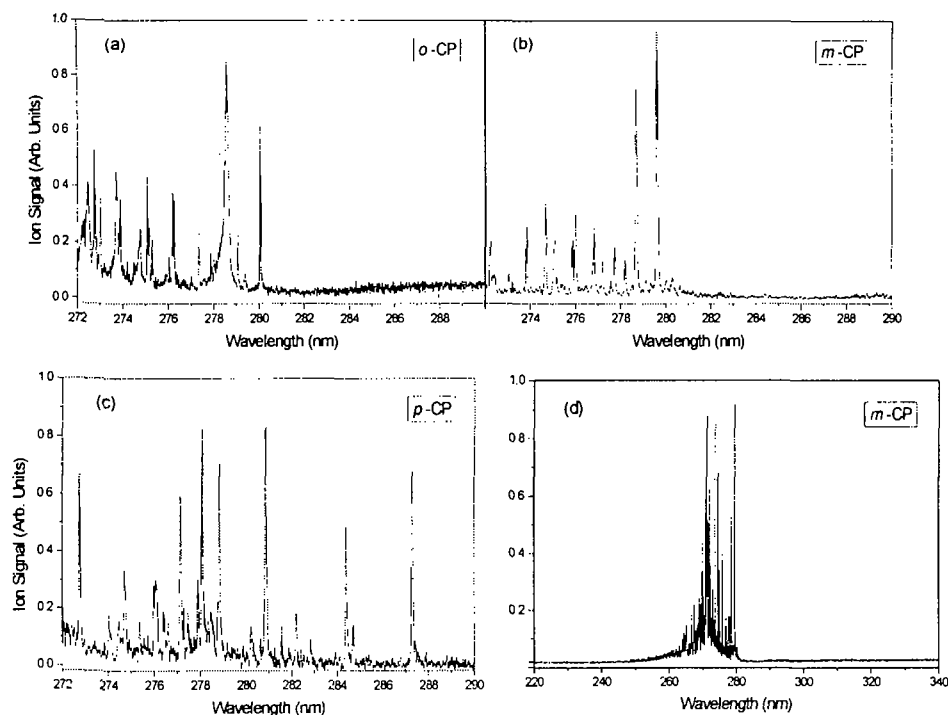


Figure 1: REMPI spectra of (a) *o*-, (b) *m*- and (c) *p*-chlorophenol in the wavelengths range 272-290 nm. in (d) the REMPI spectrum of *o*-chlorophenol is shown in the wavelengths range 220-340 nm.

The REMPI spectra of the dichlorophenols are shown in figure 2. It has been reported that dichlorophenols which have chlorine atom substitution in the ortho position cannot be measured in a two-photon ionization process⁴. Although, the sharp structured $S_1 \leftarrow S_0$ transition cannot be observed for 2,6-dichlorophenol, a few sharp peaks of relatively low intensity can be resolved for the 2,3- and 2,4-dichlorophenols. More pronounced peaks were obtained for 2,5-dichlorophenol. Literature data suggest that 2,4-dichlorophenol is a suited PCDD/F surrogate compound (for waste incineration flue gases) as a close relationship between the I-TEQ-value and the concentration of 2,4-dichlorophenol in the flues gas was observed³. The ionization efficiency of the dichlorinated phenols seems to be significantly lower than the one of the monochlorinated species.

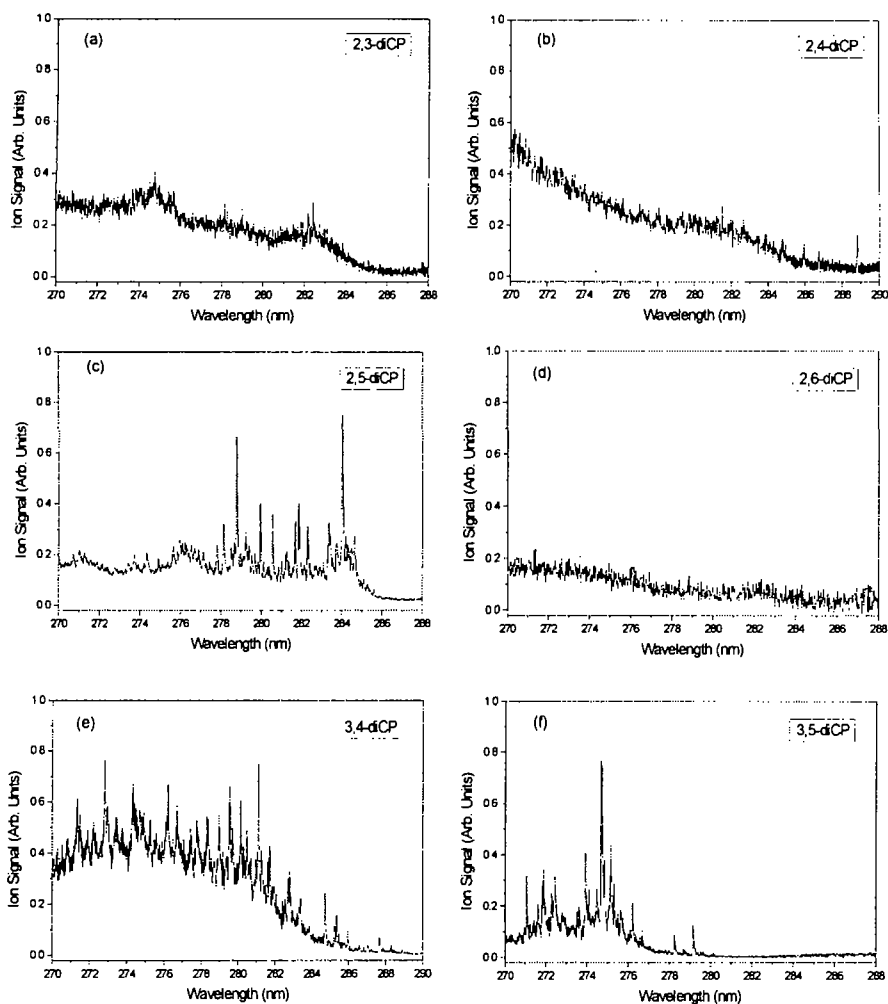


Figure 2 REMPI spectra of (a) 2,3-, (b) 2,4-, (c) 2,5-, (d) 2,6-, (e) 3,4- and (f) 3,5-dichlorophenol.

Figure 3 shows the REMPI spectrum as well as the REMPI mass spectrum of 2,4,5-trichlorophenol. All trichlorophenols including 2,4,5-trichlorophenol can be detected by REMPI-TOFMS. The REMPI-spectra, however, do not reveal any sharp UV-spectroscopic transitions. The trichlorophenols exhibit very poor REMPI-ionization efficiencies. This is due to the “heavy atom effect” which causes extremely short excited state lifetimes (i.e. population of the triplet manifold due to *inter system crossing*, ISC). In summary, both the REMPI-detection efficiency and the resolvable vibronic structure in the REMPI spectra decreases for the chlorophenols rapidly with increasing number of chlorine substituents.

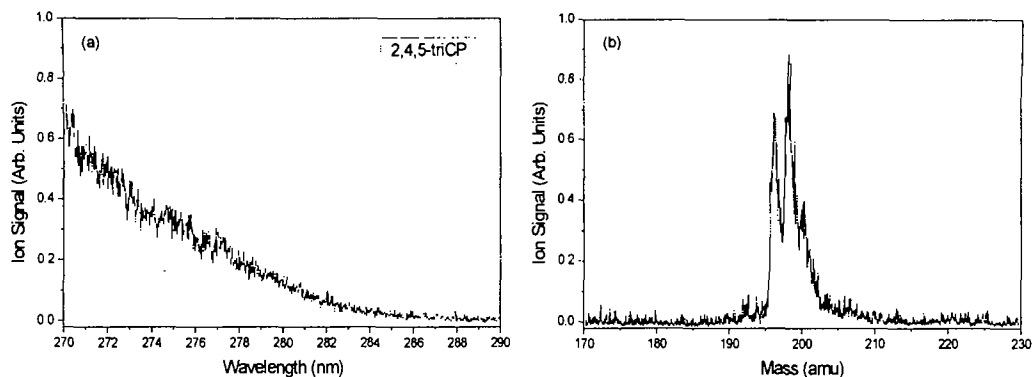


Figure 3: REMPI spectrum (a) and mass spectrum (b) of 2,4,5-trichlorophenol.

Conclusion

In this study, the sharp structured S_1 vibronic transitions could be measured in the REMPI-spectra of all mono and dichlorophenols except 2,6-dichlorophenol. Although the efficiency of the REMPI process was not distinctly investigated within this study, it can be expected that at least the monochlorinated phenols might be on-line detectable by REMPI-TOFMS in incinerator flue gases. Another possibility is the use of a two-color process^{7,8} or the application of short pulse lasers (fs/ps-pulses)⁹ to ionize chlorophenols more efficiently.

Acknowledgments

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