

Resonance-Enhanced Multi-Photon Ionization (REMPI)/Mass Spectrometry for Analysis of Chlorinated Compounds: The First REMPI Spectrum of a Chlorinated Dibenzofuran

R. Zimmermann^{1,2}, D. Lenoir², K.-W. Schramm², A. Kettrup², U. Boesl¹

- 1 Institut für Physikalische und Theoretische Chemie
Technische Universität München
Lichtenbergstr. 4, D-85747 Garching, Germany
- 2 Institut für Ökologische Chemie
GSF-Gesellschaft für Umwelt und Gesundheit GmbH
Ingolstädter Landstr. 1, D-85758 Oberschleißheim (Neuherberg), Germany

1 Abstract

Resonance-enhanced laser mass spectrometry (i.e. the combination of resonance-enhanced multi-photon ionization with lasers and time-of-flight mass spectrometry) represents a two dimensional analytical method.

In this work the highly resolved UV spectrum -measured by resonance-enhanced two-photon ionization (REMPI)- of 2,8-dichlorodibenzofuran is presented. The spectrum is characterized by a distinct, isomer-specific vibronic finestructure. This demonstrates that resonance-enhanced laser mass spectroscopy allows substance- and even isomer-selective detection of PCDF out of complex mixtures.

2 Introduction

It has been shown previously that the combination of resonance-enhanced multi-photon ionization (REMPI) and time-of-flight mass spectrometry (TOF) is a two dimensional method (ionization laser wavelength- and molecular mass-dimension) for substance- and even isomer-selective determination of organic compounds out of complex matrices /1/. However a prerequisite for selective ionization is a well structured REMPI spectrum (i.e. high resolution UV spectrum measured via REMPI) of the compound to be analyzed. Due to the recent character of the method the REMPI spectra only of some hundred compounds have been measured till now. Our group (TU München) has shown the applicability of the method for isomer-selective ionization and detection of chlorinated benzenes (PCBz) /2/, chlorinated biphenyls (PCB) /3/, chlorinated dibenzodioxins (PCDD) /4/ and chlorinated PAH's (PC-PAH) /5/. Also first applications for time resolved on-line emission monitoring of exhaust gas /6/ (automobil engine) have been performed.

Here we would like to present the first REMPI results for an chlorinated dibenzofuran.

3 Experimental

The experimental setup as well as the principle of resonance-enhanced laser mass spectrometry has been described elsewhere [7]. Briefly, the setup consists of an excimer pumped dye laser (tunable laser radiation), a frequency quintupled Nd:YAG laser (213 nm laser radiation) and a time-of-flight mass analyzer with a special, heatable sample inlet system for generation of a supersonic molecular beam. The principle of resonance-enhanced laser ionization is as follows:

The sample is vaporized and seeded in argon within a heated inlet valve. This probe gas is injected into the vacuum through a pinhole in a pulsed way, creating a supersonic molecular beam (jet). During the expansion the vibrational temperature of the molecules in the molecular beam is cooled (10-30°K) effectively. As a consequence of the cooling the UV spectra of even larger aromatic compounds show a extremely sharp structured vibrational substructure (spectral resolution of modern IR spectroscopy or better, see fig. 2 and 4). In the ion source the molecular beam is intersected synchronously by the dye laser and the Nd:YAG laser (213 nm) pulses. If the wavelength of the tunable dye laser is in resonance with a specific UV spectroscopic transition of a substance in the jet, these molecules absorb photons. Other substances -having other UV spectroscopic properties- do not absorb photons. In a second step only the selectively excited molecules are ionized by absorption of a further photon. The so formed ions are detected in the time-of-flight mass spectrometer. By registering the ion yield (mass selected in TOF) as a function of the laser wavelength one obtains the REMPI spectrum (i.e. a UV spectrum measured via ion current). Figure 1 shows a schematic time-of-flight spectrometer with the inlet system for supersonic jet cooling.

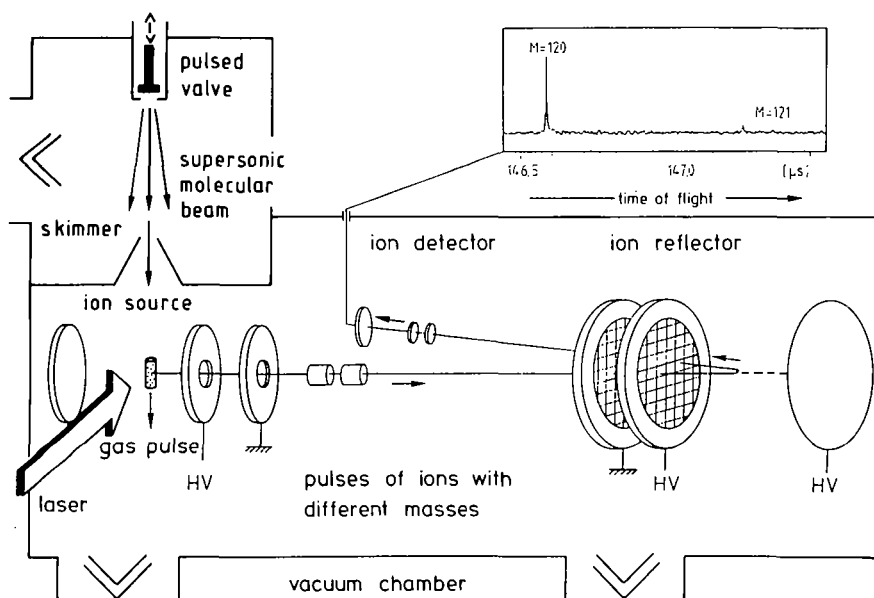


Figure 1

Schematic representation of a modern laser mass spectrometer: The sample molecules are cooled in a supersonic jet expansion. The formed molecular beam is intersected by the ionization laser(s). The generated ions are mass analyzed in the time-of flight mass spectrometer. The ion reflector compensates initial energy distributions and therefore allows high mass resolutions (10000 and more, 5000 all-day) in combination with high transmission rates.

For the compound under investigation the excitation energy of the first excited singlet state is lower than half the ionization potential. Therefore the excited 2,8-DCDF can not be ionized by another dye

laser photon absorption (i.e. the energy of two dye laser photons is smaller than the ionization energy). However, this problem can be managed by synchronous irradiation of laser light with a sufficiently short wavelength ("two-color" ionization) /8/. For our experiments we used a frequency doubled dye laser beam in the 299-315 nm range with a pulse energy of about 300 μ J (Rhodamine B dye) for the excitation step and Nd:YAG generated 213 nm laser light with an approx. pulse energy of 100 μ J for the ionization step /2/.

4 Results

The REMPI spectrum (i.e. highly resolved UV spectrum) of the first singlet transition ($^1A_1 \leftarrow ^1A_1$ in C_{2v} symmetry /9/) of 2,8-dichlorodibenzodioxin (2,8-DCDF) is presented in figure 2. The vibrationless transition is located at 311.85 nm. The spectrum shows a well resolved vibronic finestructure. Some spectroscopic data of 2,8-DCDF and dibenzofuran are tabulated in table 1.

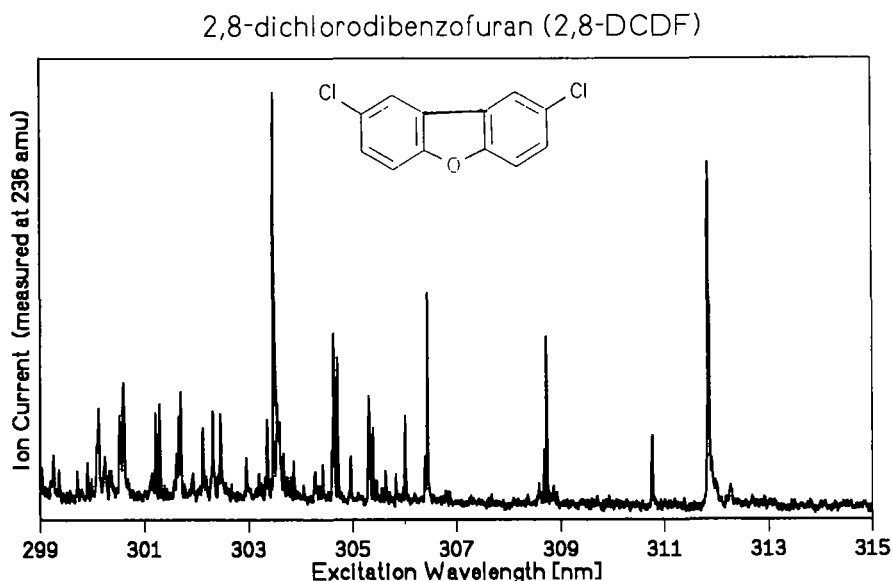


Figure 2

Highly resolved UV-spectrum of jet cooled 2,8-dichlorodibenzofuran, measured by resonance-enhanced multi-photon ionization spectroscopy (REMPI). The spectrum has been recorded mass selectively for $M=236$ amu (all- ^{35}Cl isotopomer)

Table 1

Some spectroscopic properties of dibenzofuran and 2,8-dichlorodibenzofuran

compound	exp. IP_1	IP (AM1)_2	$\text{IP (AM1-corrected)}_3$	UV-spect. origin ₄
dibenzofuran	7.9 [eV]	8.94 [eV]	7.9 [eV]	297.30 [nm]
2,8-DCDF	-	9.23 [eV]	8.19 [eV]	311.85 [nm]

1 measured by photoelectron spectroscopy /10/

2 calculated with the AM1 hamiltonian (HyperChem 3.0 molecular orbital program)

3 the difference between the calculated IP value and the experimental result for dibenzofuran (1.04 eV) has been taken as off-set constant /11/

4 the UV spectroscopic origin from dibenzofuran has been taken from ref. /4/

The selectivity of resonance-enhanced laser mass spectrometry is demonstrated in figure 3. A mixture of 1,4-dichloronaphthalene, 2-chlorodibenzo-p-dioxin and 2,8-dichlorodibenzofuran has been filled into the inlet valve. By tuning the dye laser wavelength in resonance with a substance-specific vibronic transition of a chosen substance this compound can be ionized selectively. The mass spectra show the enhancement of the respectively selected compound.

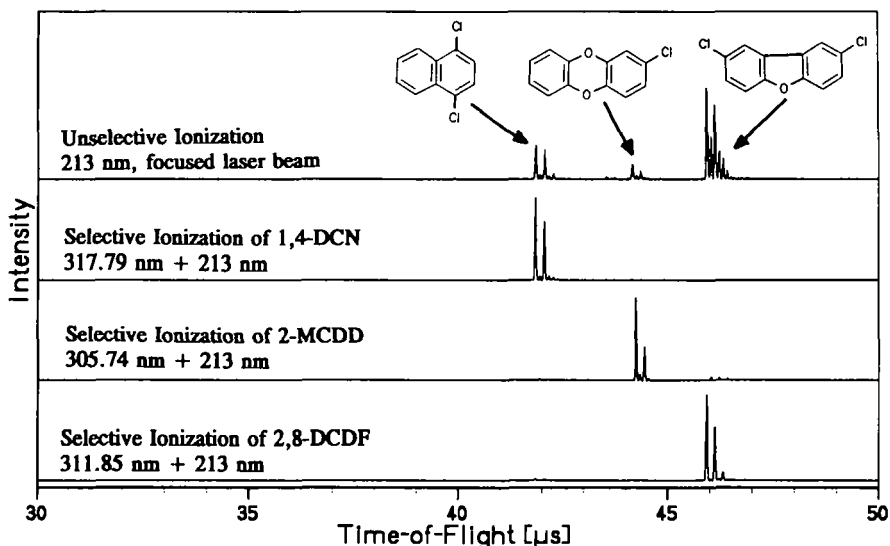


Figure 3

Substance selective ionization by resonance-enhanced laser mass spectrometry of compounds out of a mixture of 1,4-dichloronaphthalene (1,4-DCN), 2-chlorodibenzo-p-dioxin (2-MCDD) and 2,8-dichlorodibenzofuran (2,8-DCDF). The excitation wavelengths are indicated above the corresponding trace. The mass spectra also show another important feature of resonance-enhanced laser ionization, the possibility of effective but fragmentless ionization.

5 Discussion

In this work the applicability of resonance-enhanced laser mass spectroscopy for substance selective ionization and detection of chlorinated dibenzofurans is shown. The practicability of isomer selective ionization can be concluded by comparison with REMPI results obtained for other substance classes [2,4,5]. As an example the REMPI spectra of 2,7-, 2,3- and 2,8-dichlorodibenzo-p-dioxin are shown in figure 4. In comparison with the 2,8-dichlorodibenzodioxin spectrum (fig. 2) the DCDD spectra exhibit a much more dense line structure. This is due to a geometry shift between the ground- and excited state of dibenzodioxin derivatives (i.e. different folding angles) which causes the induction of progressions of low frequency inversional vibronic modes [16]. The structure of the first UV spectroscopic transition of 2,8-DCDF (distinct spaced vibronic lines in the origin region) is more similar to those of smaller PAH's [5,8] (which are planar) than those of dichlorinated dibenzo-p-dioxins [4] (which have a folded conformation). The PCDF's show planar structures in the ground and probably also in the first excited states [16]. However, isomer selectivity is easily reached for dichlorinated dibenzo-p-dioxins (see insert). Therefore isomer-selectivity should be achievable for chlorinated dibenzofurans in a equal manner or even better as for chlorinated dioxins.

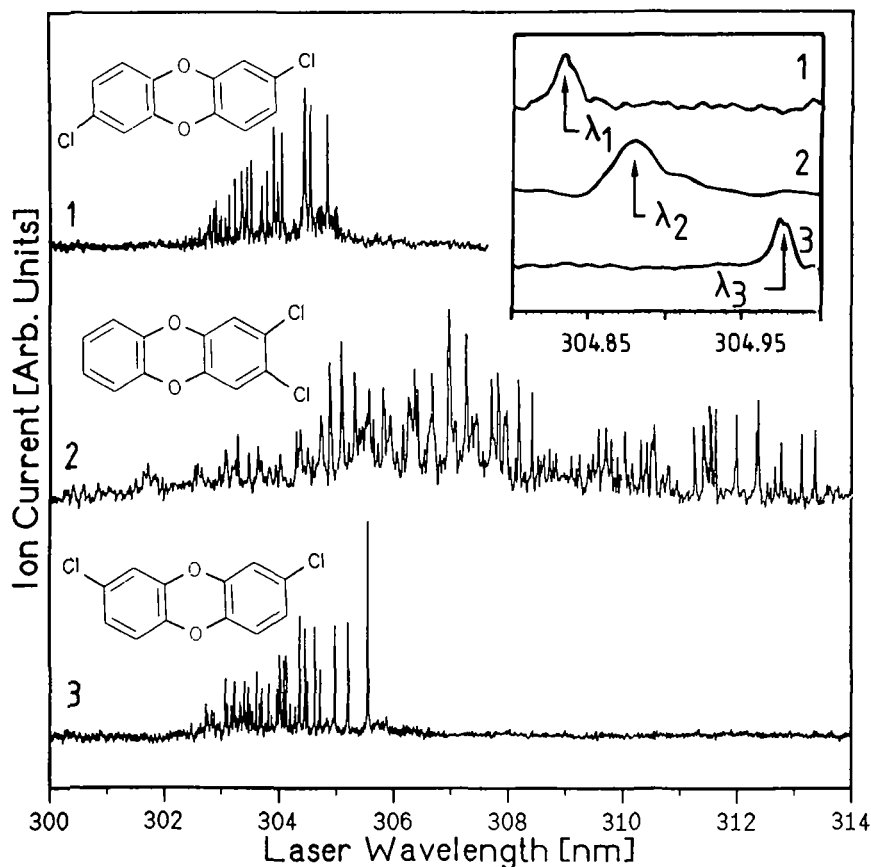


Figure 4
REMPI spectra of 2,3-, 2,7- and 2,8-dichlorodibenzo-p-dioxin /4/ (DCDD's) measured mass selectively at $M=252$ amu (all ^{35}Cl isotopomers). For demonstration of the isomer selectivity an enlarged view on the spectra is shown in the insert. Three wavelengths for isomer-selective ionization are indicated.

For different aromatic compounds detection limits in the sub-ppb range for on-line measurements /12/ as well as in the 100 fg range for (unselective) GC-laser mass spectrometry /13/ have been achieved.

For application of resonance-enhanced laser mass spectrometry on new compounds the knowledge of UV spectroscopic as well as ionization potential data is important. Hitherto these data are available only for some hundred molecules. Therefore analytical applications of resonance-enhanced laser mass spectrometry are limited to these investigated compounds so far. Nevertheless, supersonic jet spectroscopy represents a quickly expanding research topic, promising a rapid increase of the accessible spectroscopic data set. Furtheron some of the data can be obtained from conventional solution UV spectroscopy /14/ or in particular by quantum mechanical calculations (especially for calculation of IP data see the contribution submitted for this issue of Organohalogen Compounds /11/)

However, the high selectivity and sensitivity performed by resonance-enhanced laser mass spectrometry allows many analytical applications for example in the field of on-line emission monitoring of traces of pollutants in exhaust gases at present. An analytical system for time resolved measure-

ment (50 ms time resolution) of inorganic and organic pollutants in automobile exhaust gas is already realized /6/. Further work is in progress for combination of resonance-enhanced laser mass spectrometry with a fast GC preseparation (three-dimensional analytical system) for a rapid survey analysis of selected pollutants out of emission samples. Another promising application would be the on-line monitoring of indicator parameters for the occurrence of PCDD/F in exhaust gases of e.g. hazardous waste incinerators. Recent studies on this topic have shown that the emission of PCDD/F during waste incineration is well correlated with concentration of chlorinated benzenes (PCBz) or phenols (PCP) in the exhaust gas /15/.

6 Acknowledgments

We gratefully acknowledge the financial support from the DECHEMA e.V. Frankfurt, Germany (research-scholarship for R.Z.).

7 Literature cited

- /1/ U.Boesl, H.J.Neusser, E.W.Schlag, Chem. Phys.55 (1980) 193
R.Trembreull, C.H.Sin, P.Li, H.M.Pang, D.M.Lubman, Anal. Chem. 57 (1985) 1186
D.M.Lubman, Anal. Chem.59 (1987) 31A
V.S.Letokhov, Laser Photoionization Spectroscopy, Academic press, Orlando FL (1987)
- /2/ C.Weickhardt, R.Zimmermann, K.-W.Schramm, U.Boesl, E.W.Schlag, Rapid Commun. Mass. Spectrom. 8 (1994) 381
- /3/ R.Zimmermann, C.Weickhardt, U.Boesl, E.W.Schlag, accepted for publication in J. Molec. Struct. (1994)
- /4/ C.Weickhardt, R.Zimmermann, U.Boesl, E.W.Schlag, Rapid Commun. Mass Spectrom. 7 (1993) 183
R.Zimmermann, U.Boesl, C.Weickhardt, D.Lenoir, K.-W.Schramm, A.Kettrup, E.W.Schlag accepted for publication in Chemosphere (1994)
- /5/ R.Zimmermann, C.Lerner, K.-W.Schramm, D.Lenoir, U.Boesl, to be published in RIS 94 Conferencr-proceedings, AIP-press, (1994)
- /6/ U.Boesl, C.Weickhardt, R.Zimmermann, S.Schmidt, H.Nagel, SAE Technical Paper Ser. 930083 (1993)
C. Weickhardt, U.Boesl, E.W.Schlag, Anal. Chem. 66 (1994) 1062
- /7/ U.Boesl, R.Weinkauff, E.W.Schlag, Int. J. Mass. Spectrom. Ion Processes 112 (1992) 121
U.Boesl, R.Zimmermann, C.Weickhardt, D.Lenoir, K.-W.Schramm, A.Kettrup, E.W.Schlag accepted for publication in Chemosphere (1994)
- /8/ J.W.Hager, S.C.Wallace, Anal Chem. 60 (1988) 5
- /9/ The assignment of the electronic transition is due to a AM1-CI molecular orbital calculation (using 33 singly excited configurations in the CI), performed with thw HyperChem 3.0 program
- /10/ J.H.D.Eland, J. Mass. Spectrom. Ion Phys. 2 (1969) 471
- /11/ R.Zimmermann, submitted for this issue of Organohalogen compound
- /12/ B.A.Williams, T.N.Tanada, T.A.Cool, 24th International Symposium on Combustion/The Combustion Institute (1992) 1587
E.A.Rohlfing, 22nd Internat. Symposium on Combustion/The Combustion Institute (1988)
- /13/ G.Rhodes, R.B.Opsal, J.T.Meek, J.P.Reilly, Anal. Chem. 55 (1983) 280
- /14/ as example for higher chlorinated dibenzofurans: M.Tysklind, K.Lundgren, C.Rappe, Chemosphere 27 (1993) 535
- /15/ A.Kaune, D.Lenoir, U.Nikolai, Organohalogen Compounds Vol. 12 (1993) 39
- /16/ R.Zimmermann, unpublished results