

REMPI-SPECTROSCOPY OF DIBENZO-P-DIOXIN AND ITS CHLORINATED ISOMERS: IMPLICATION FOR ANALYTICAL APPLICATIONS OF THE REMPI-TOFMS TECHNIQUE

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Introduction

In the last years, the laser based resonance-enhanced multiphoton ionization-time-of-flight mass spectrometry (REMPI-TOFMS) technique [1-3] was successfully applied for on-line monitoring of products of incomplete combustion (PIC) in flue gases of industrial combustion processes. This included the measurement of precursors/surrogates for polychlorinated dibenzo-p-dioxins (recent investigations pointed out that there are valid surrogate compounds for dioxin-emission from waste incineration, i.e. monochlorobenzene [4] and some non chlorinated aromatic species during "memory" emission phases [5]). Furthermore REMPI-measurements of polycyclic aromatic hydrocarbons (PAH) [4-6] and other compounds like NO or NH₃ have been reported. It is obvious that a direct on-line measurement of the *international toxicity equivalent* (I-TEQ) value of PCDD/F is beyond recent on-line monitoring concepts (if on-line stands for real-time). Thus it is decisive for future application of the REMPI-TOFMS technique in the field of "dioxin-emission control" to identify the most suitable PCDD/F surrogates. Candidate molecules need to be evaluated regarding both, the I-TEQ correlation and the physical-chemical prerequisites for on-line monitoring (i.e. REMPI-spectroscopic properties) [7]. In this context this paper deals with the REMPI-spectroscopic properties of the dibenzo-p-dioxin (DD) molecule and its monochlorinated derivatives (MCDD) and the general problems arising upon REMPI ionization of chlorinated species. These compounds are investigated by means of REMPI-TOFMS with supersonic jet inlet (Jet-REMPI-TOFMS or Jet-REMPI) and INDO/S-CI quantum chemical calculations. The 2+2 four-photon REMPI-spectrum of the S₁(¹B₁)/S₂(¹A₁) systems of DD is presented and compared with the 1+1 REMPI-spectrum. Additionally the 1+1 REMPI-spectra of 2- and 1-monochlorodichloro-p-dibenzo-p-dioxin are presented and interpreted regarding spectroscopic and analytical aspects. Furthermore, a two color-REMPI scheme for detection of higher chlorinated species, based on REMPI spectroscopic results on 2,8-dichlorodibenzofuran is presented and discussed.

Experimental

An tunable dye laser pumped by the output of an excimer laser and a homebuilt time-of-flight mass analyzer (TOFMS) with a supersonic jet inlet system were used. A detailed description of the REMPI-TOFMS technique and instrumentation is given in the literature [8]. Briefly the 2+2-REMPI spectrum of dibenzo-p-dioxin (DD) was recorded by focusing the output of a dye-laser (Rhodamin 6G, 7mJ/pulse, f_{lens} = 100 mm) onto the supersonic molecular beam in the ion source of

the TOFMS. Very hard focusing conditions were necessary for enforcement of the critical non-resonant two-photon absorption step. However, massive fragmentation of the formed DD ions occurs under these conditions, due to multiple photon absorption by the formed molecular ions. In the mass spectrum the C^+ -peak ($m=12$ m/z) is by far most abundant and accompanied by only some larger fragment peaks of minor intensity (no molecular mass peak). The 2+2 REMPI spectrum of dibenzo-p-dioxin was thus recorded via the C^+ mass signal. The one-photon resonant, two-photon ionization spectra (1+1-REMPI) of dibenzo-p-dioxin as well as of the monochlorinated congeners (1- and 2-MCDD) were recorded via the molecular mass peak using the frequency doubled, unfocused output of the dye laser. For experimental details on the two color ionization of 2,8-dichlorodibenzofuran see reference [12]. The quantum chemical calculations were performed with the INDO/S-CI method [9], implemented in the HYPERCHEM program package.

Results And Discussion

Quantum chemical INDO/S-CI calculations depict, that the energy gap between the first two excited singlet states (S_1 and S_2) of the dibenzo-p-dioxin molecule (DD) is small (~ 600 cm^{-1}).

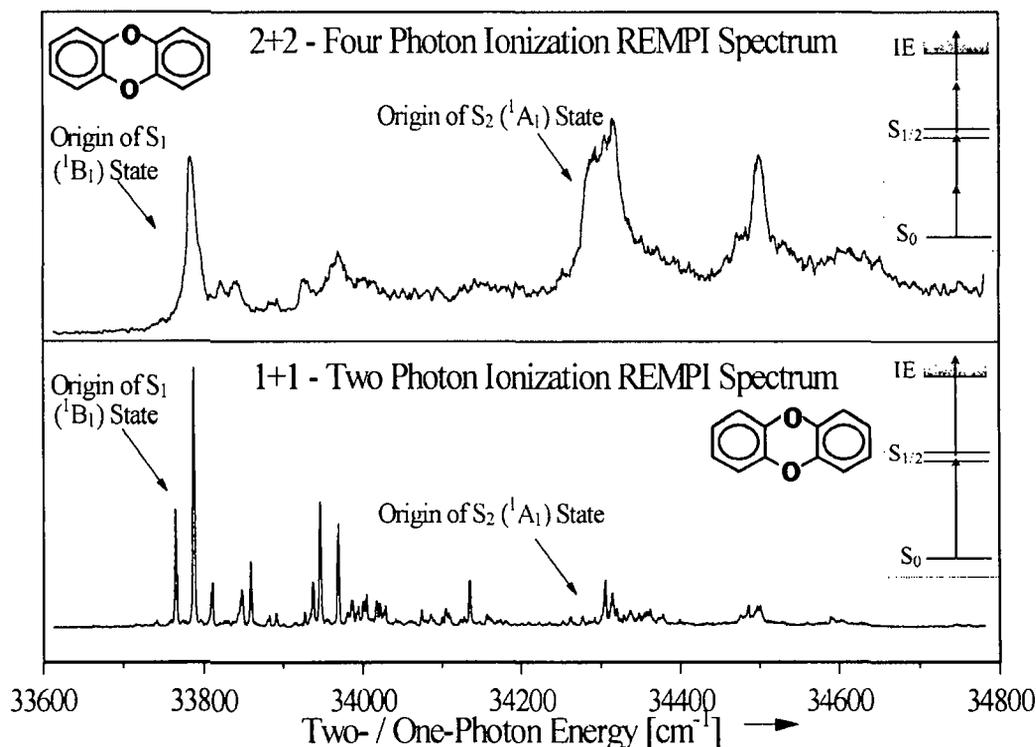


Figure 1: Four-photon (2+2, top) and two-photon (1+1, bottom) REMPI-spectra of dibenzo-p-dioxin (DD). Due to the differences in the electronic selection rules, the two photon absorption experiment (2+2-REMPI, top) shows the S_2 -band system more intense than the one-photon experiment (1+1-REMPI, bottom). IE means ionization energy (\sim ionization potential), S_1 stands for first, S_2 for second excited singlet state and S_0 for ground state.

The S_1 transition of DD is electronically allowed (1B_1 , INDO/S-CI energy: 34490 cm^{-1}), but predicted to be rather weak (INDO/S oscillator strength $f=0.05$). The second singlet transition (S_2 ,

1A_1 , INDO/S: 35090 cm^{-1} , $f=0$) is electronically forbidden for a planar (D_{2h}) DD geometry. However, due to the slightly folded structure of DD (C_{2v}), the S_2 transition gains some electronically allowed character (although being extremely low, the INDO/S calculations predict a very weak oscillator strength of $f\sim 0.001$ for 12° folding angle). The very weak oscillator strength of the S_2 transition makes it impossible to identify the band of the S_2 -system within the higher S_1 vibronic transitions in the UV absorption spectrum (i.e. the conventional 1+1 REMPI spectrum). However, as for both states, the S_1 and the S_2 , the two photon absorption is electronically allowed, a two-photon resonant, four photon ionization REMPI-spectrum (2+2-REMPI) of DD reveals the origin band of the S_2 -system more clearly. Figure 1 shows the 1+1 (lower trace) and 2+2 REMPI spectra of DD (upper trace). The short progression of the low frequency butterfly mode visible in the 1+1 REMPI spectrum (i.e. the first three peaks with a spacing of 23 cm^{-1}) indicate a small change of the folding angle upon the $S_0\rightarrow S_1$ - transition. This corresponds to results from quantum chemical investigations [10, 11] which support a planar structure in the S_1 state, and a slightly folded geometry in the S_0 (folding angle: 12.2° , *ab initio* HF calculation, 6-31G* [11]). A more detailed analysis of the 1+1 REMPI-spectrum is given in ref. [11]. The upper trace shows the 2+2 REMPI spectrum. The first intense peak ($\sim 33800\text{ cm}^{-1}$) is due to the origin region of the (two-photon allowed) S_1 system while the second intense peak ($\sim 34300\text{ cm}^{-1}$) represents the origin of the two-photon allowed S_2 -system.

However, the very high laser intensities necessary for recording of the 2+2 REMPI spectrum induce power broadening effects make a detailed analysis of the vibronic structure impossible. In the 1+1 spectrum, one can recognize some small peaks in the S_2 origin region, suggesting a very weak oscillator strength for the S_2 one-photon transition, as predicted by the quantum chemical calculations for a slightly folded geometry of DD in the S_0 ground state.

Figure 2 shows the REMPI spectra of 1- and 2-monochlorodibenzo-p-dioxin. Due to the disturbance of the molecular symmetry, the S_2 system gains some allowed character for these compounds. In Figure 2 (bottom) the 1+1 REMPI spectrum of 2-monochlorodibenzo-p-dioxin (2-MCDD) is depicted. The 2-MCDD S_1 origin lies at 305.9 nm , the S_2 band origin system is observable at 301.8 nm (predicted S_2/S_1 relation INDO/S: 1/5). For a more detailed vibronic analysis of the 2-MCDD spectrum see ref. [11]. For other non-symmetric substituted PCDD congeners like 2,3-dichlorodibenzo-p-dioxin the S_2 system is clearly also observable in the 1+1 REMPI spectrum [10]. Surprisingly it was not possible to achieve a 1+1 REMPI spectrum of the S_1 and S_2 transitions of the 1-monochlorodibenzo-p-dioxin (1-MCDD) with sharply resolved vibronic transitions. Figure 2 (top) shows the obtained 1+1 REMPI spectrum of 1-MCDD. Only two very weak and broadened band systems (y-axis considerably exaggerated for 1-MCDD in Figure 2), which most likely represent the S_1 and S_2 transitions, are observable in the REMPI spectrum. Apparently, the chlorine substitution in the ortho-position to the ether-bridge quenches the REMPI-process. This "ortho-effect" may be due to an intra-molecular interaction between the (*d*-orbitals of the) chlorine substituent and the (*p*-orbitals of the) oxygen atom that favors either a rapid deactivation of the S_1 excitation (further increased inter system crossing, ISC rate or internal conversion, IC) and/or a large geometry shift upon excitation. If this effect is general for PCDD, the consequence would be that PCDD which are chlorinated in the 1,4,6 or 9 position can not be efficiently ionized by REMPI via their S_1 and S_2 states. All toxic penta- through octa- chlorinated congeners (2,3,7,8-PCDD) would, therefore, be excluded from selective REMPI detection. Furthermore, it is likely

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that the same effect occurs for dibenzofurans which are chlorinated in the 4 or 6 position. In addition to the above mentioned adverse effects of chlorine substitution in ortho-positions to the oxygen atoms, drastic quenching of the ionization efficiency is induced by the inter system crossing (ISC) mechanism (note that the ISC rate for highly chlorinated compounds is already very high without considering the hypothetical effects of Cl and O in ortho position on the ISC rate). The ISC-process is an iso-energetic transition from the excited singlet state (here: S_1 or S_2) to the first triplet state (T_1), and is favored by the presence of heavy atoms like chlorine (due to the increase of electronic spin-orbit coupling, which is a relativistic effect occurring in the close proximity of electrons and heavy atom nuclei).

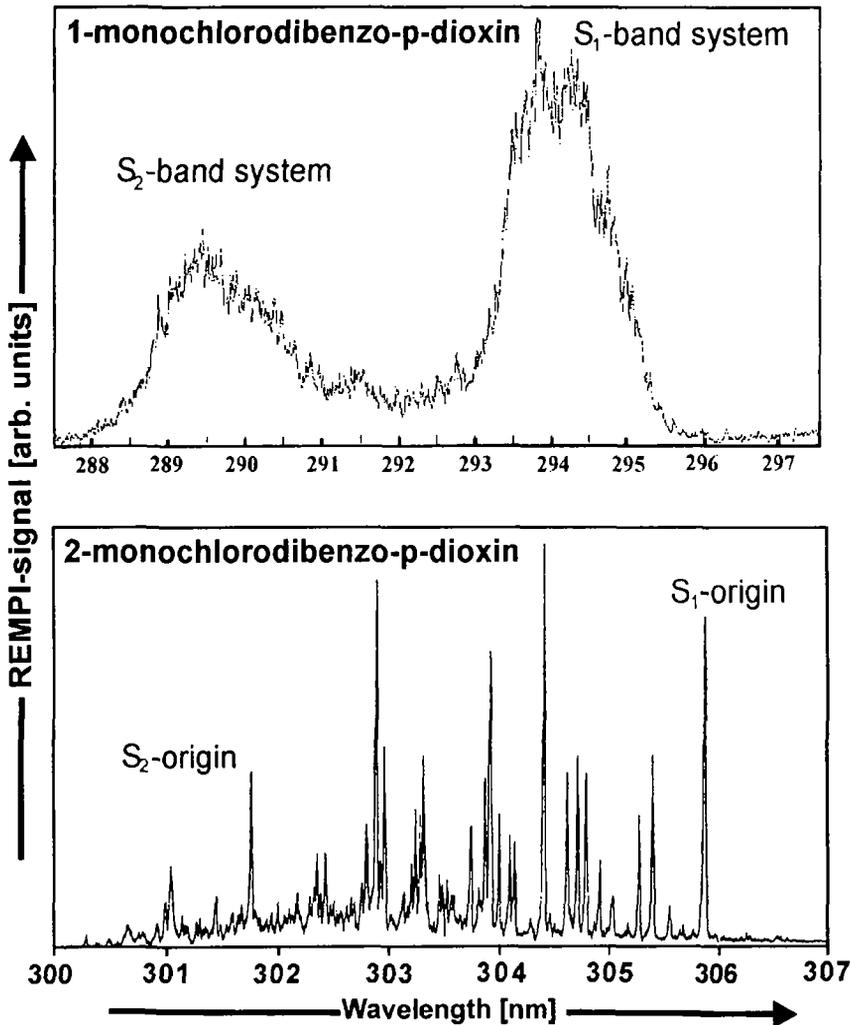


Figure 2: REMPI spectra of 1- and 2-monochlorodibenzo-p-dioxin

As the energy of the first triplet state ($E_{T_1 \text{ origin}}$) is considerably lower with respect to the S_1 or S_2 state origins ($\sim 1-2.5$ eV), the first triplet state (T_1) state is highly vibrationally excited (hot) after

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the ISC process ($E_{\text{vib}} = E_{\text{exc. } S_1} - E_{T_1 \text{ origin}}$). This high vibrational excitation avoids the straightforward postionization from the T_1 (which in principle is possible from an energetic point of view), as the *Franck Condon* propensity rule needs to be satisfied. The *Franck Condon* propensity rule states that the electronic transition probability is maximal, if the electronic origin state and the electronic final state exhibit the same vibrational quantum state (under the prerequisite that there are no significant changes in the molecular structure upon the electronic transition). On the other hand, the transition probability can be totally suppressed if the difference of the vibrational quantum state of origin and final state is very large. This rule has implications on the REMPI detection of PCDD/F. As mentioned above, the PCDD/F molecule undergoes rapid ISC after the excitation step (absorption of the first photon). The resulting highly vibrational excited PCDD/F molecule in the triplet state cannot be ionized by an additional photon absorption (even when a one-color ionization is formally possible) due to the mismatch in the vibrational quantum states (no *Franck Condon* overlap).

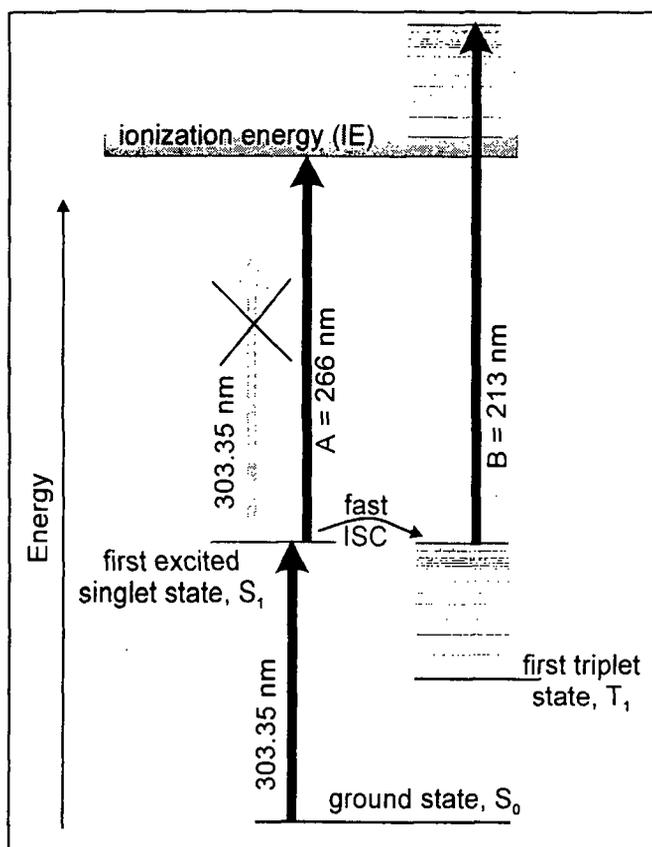


Figure 3: Two color ionization scheme for REMPI detection of PCDD/F congeners (after an experiment on 2,8-dichlorodibenzofuran [11,12]). See text for explanation.

In order to post ionize the “hot” PCDD/F species from the triplet state, a photon of considerably higher energy (shorter wavelength) is required. For efficient post ionization, the energy of the photon should exceed the formally required energy for ionization of the excited PCDD/F species (E_{req}).

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= $IE - E_{exc, S_1}$) by at least the internal vibrational energy E_{vib} . In Figure 3 the two-color ionization schemes, as applied for REMPI ionization of 2,8-dichlorodibenzofuran (2,8-DCDF, see reference [12]), are depicted. The S_1 -excitation of the 2,8-dichlorodibenzofuran is performed by 303.35 nm laser pulses. If 266 nm laser pulses (Figure 3, route A) are applied for the post ionization step in the two-color REMPI scheme, the "direct" route via the S_1 is preformed (i.e. the 266 nm photon absorption/ionization step starts from the excited S_1 state). Although the *Franck Condon* propensity rule is satisfied for route A, the ionization efficiency is quenched due to the fast depletion of the S_1 state by ISC. With the 213 nm photons (Figure 3, route B) the rule for post ionization from the highly vibrationally excited T_1 state is fulfilled. Considerably enhanced ionization yields are achieved for 213 nm post ionization with respect to 266 nm post ionization. In detail, a six fold increase of the ionization efficiency was achieved with 213 nm, although the pulse energy of the 213 nm pulses was only 1/3 of the 266 nm pulse energy.

A two-color REMPI scheme based on post ionization of the PCDD/F from the triplet manifold with relative high photon energies may be a solution for some of the recently proposed analytical REMPI applications on chlorinated species (e.g. chlorinated benzenes (PCBz), phenols (PCPh) or some PCDD/F species). However it has to be considered that for REMPI-TOFMS on-line monitoring applications on real world samples (flue gasses etc.), post ionization with rather "blue" photons cause an increased background signal due to co-ionization unwanted molecular species like PAH.

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