

Analytical Possibilities of the Fine-Structure Phosphorescence Spectrometry Technique for Registration of Polychlorinated Dioxins

V. G. Klimenko^{1,2} and R. N. Nurmukhametov¹

Received October 27, 1997; accepted December 23, 1997

The fine-structure phosphorescence spectra of 11 chlorinated dibenzo-*p*-dioxins were registered in hexane solutions at 77 and 4.2 K. Vibronic structure peculiarities were revealed and the possibility of its analytical application was demonstrated. Evaluation of the detection limit for dioxin was performed for our spectral equipment.

KEY WORDS: Dioxin; fine-structure; phosphorescence; spectrum.

INTRODUCTION

It is known that as a result of industrial activity, the environment in many regions is polluted with polychlorinated dibenzo-*p*-dioxins (PCDD). Dioxins are highly toxic substances, with their various isomers having different orders of toxicity. In this connection, for the detection of PCDD it is necessary to ensure the high selectivity of the method. For the determination of trace concentrations of organic compounds, the method of chromatography-mass spectrometry is used. Among the drawbacks of this method, the high cost of the equipment, long time required for analysis, and insufficient selectivity should be mentioned. All this makes urgent research aimed at the development of new analytical methods.

The quasi-linear spectral method (Shpolskii method) is proved to be effective for analysis of luminescent organic compounds. It is well developed for analysis of the content of polycyclic aromatic hydrocarbons. However, it has not been applied to the analysis of dioxin so far, and there was a lack of data on dioxin

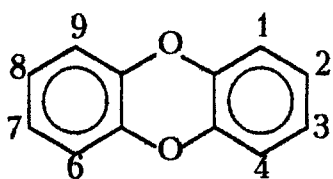
quasi-linear spectra in the literature. It was known that solid solutions of some dioxins had phosphorescence and fluorescence. The latter is much weaker and is registered in a relatively "inconvenient" UV region for analytical purposes. Phosphorescence spectra of typical dioxins are registered in a band of 380–450 nm, suitable for spectral analysis.

We have been conducting investigations to explore the possibilities of registering fine-structure spectra of PCDD, to reveal the conditions under which such spectra would have reasonably resolved vibration structures and to estimate their usefulness for molecular analysis. At the same time it was important to reveal special features in fine-structure phosphorescence spectra characteristic for every isomer.

Recently [3] we obtained fine-structure phosphorescence spectra of 2,3,7,8-tetra- and 1,2,3,7,8-pentachlorodibenzo-*p*-dioxins at the liquid helium temperature (4.2 K) in hexane matrices. Fine-structure phosphorescence spectra of unsubstituted dibenzo-*p*-dioxin (DD) at 4.2 K with detailed vibration analysis are described in Ref. 4. In Ref. 5 it was reported that phosphorescence spectra of DD were of a fine structure even at 77 K, and the best resolution was achieved in *n*-hexane and *n*-heptane matrices. In the present work we report the results

¹ L. Ya. Karpov Institute of Physical Chemistry, Vorontsovo Pole 10, Moscow 103064, Russia.

² To whom correspondence should be addressed. e-mail: klim@cc.nifhi.ac.ru



Scheme I

of a phosphorescence spectral study of hexane solutions of 12 chlorinated dioxins at 77 and 4.2K.

EXPERIMENTAL AND DISCUSSION

The phosphorescent spectra of the following set of compounds were studied: 2-chloro (2-CDD)-, 2,3-dichloro (2,3-DCDD)-, 2,3,8-trichloro (2,3,8-TrCDD)-, 2,3,7,9-tetrachloro (2,3,7,9-TCDD)-, 2,3,8,9-tetrachloro (2,3,8,9-TCDD)-, 2,3,7,8-tetrachloro (2,3,7,8-TCDD)-, 2,4,7,9-tetrachloro (2,4,7,9-TCDD)-, 1,2,3,7,8-pentachloro (1,2,3,7,8,-PeCDD)-, 1,2,3,4,7-pentachloro (1,2,3,4,7-PeCDD)-, 1,2,3,4,7,8-hexachloro (1,2,3,4,7,8-HCDD)-, 1,2,3,6,7,8-hexachloro (1,2,3,6,7,8-HCDD)-, and octachlorodibenzo-*p*-dioxin (OCDD) at 77 and 4.2 K. Positions of chlorine atoms are given in correspondence with their numeration in Scheme I. The compounds under study were synthesized using techniques described in the literature [1]. Spectra were recorded with an SDL-1 spectrometer; the excitation of phosphorescence was performed with the 313-nm line of a mercury lamp (DRSh-250). The spectral slit width of the registration monochromator did not exceed 0.05 nm. Dioxin concentrations in the studied solutions were ca. 10^{-5} M.

For 11 investigated compounds quasi linear phosphorescence spectra were successfully obtained at both 77 and 4.2 K. Only the spectrum of 1,2,3,4,5-PeCDD has the form of a broad structureless band with a maximum at 480 nm. Formerly it has been reported [1] that 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TCDD) in EPA solution at 77 K has a similar spectrum, with the maximum at 485 nm. A feature of 1,2,3,4,5-PeCDD and 1,2,3,4-TCDD is that in these molecules one benzene ring is totally chlorinated, whereas the second ring either contains no chlorine atoms (1,2,3,4-TCDD) or contains only one chlorine atom (1,2,3,4,5-PeCDD). Perhaps the cause of the structureless shape and bathochromic shift of the phosphorescent spectra of these compounds is that radiative centers are dimers but not molecules. Molecules of such compounds usually have a large dipole

moment. It is known that polar aromatic molecules with oxygen are formed in saturated hydrocarbons, as dimers.

All spectra have a strongly pronounced vibronic structure and consist of several multiplet components. Only lines of one or two components prevail in the spectra. Half-widths of lines in the spectra are 2.0–4.0 nm at 77 K and 0.2–0.5 nm at 4.2 K. At the nitrogen temperature the spectra consist of an average of 15 quasi-lines, and at 4.2 K their number mounts to several tens. Positions of the main lines of investigated compounds are listed in Table I, and phosphorescence spectra of four dibenzo-*p*-dioxin tetrachloro isomers in *n*-hexane at 4.2 K are presented in Figs. 1–4.

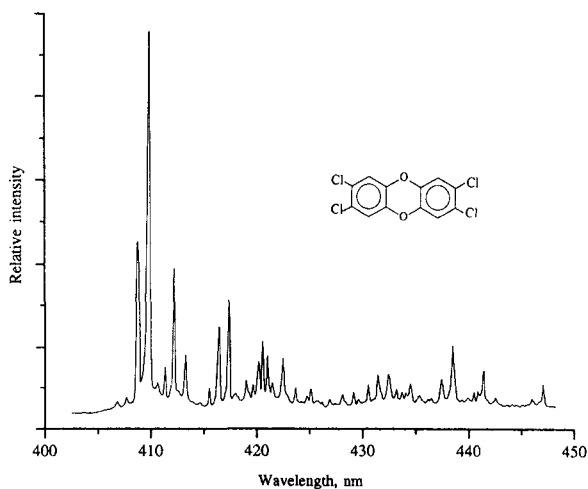
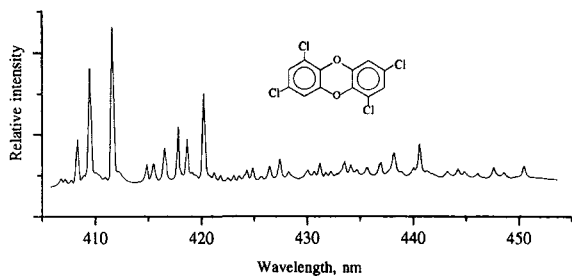
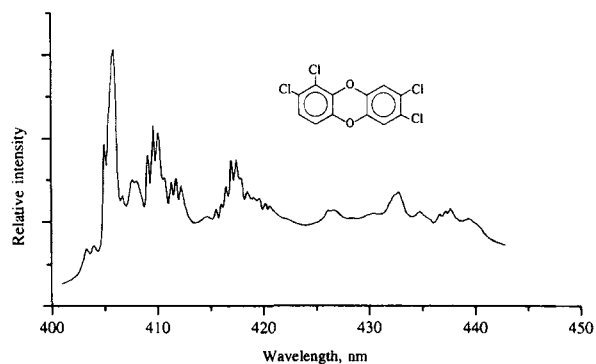
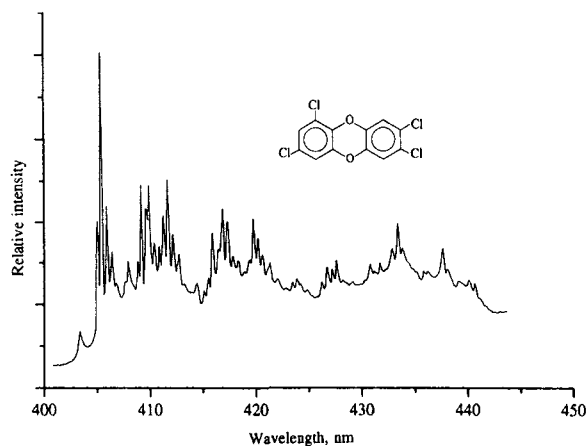
The investigations performed indicate that quasi-linear spectra of various dioxin chlorine derivatives contain a great number of distinctions. First, there are distinctions in the position of the 0–0 transition and of the spectrum as a whole. Substitution of H atoms in DD by Cl causes bathochromic shift of the $T_1 \rightarrow S_0$ transition. Thus, the 0–0 transition of the 2-CDD molecule is shifted by 3 nm compared with the 0–0 transition of DD, and for OCDD molecule this shift increases to 26 nm. As is clear from Figs. 1–4, the energy of electronic transition also depends on the position of substituents in the molecule.

Significant distinctions are also observed in the vibronic structure and in the intensity distribution of phosphorescence spectra of chlorinated dioxins. Analysis of the vibronic structure of the spectra leads to the conclusion that, in some cases, peculiarities in the vibronic structure of spectra are due to the differences in intramolecular interactions, responsible for the radiative transition. This leads to the differences in selection rules for vibronic transitions. In DD the lowest triplet state is a $B_{3g} \pi 1\pi^*$ state, and the structure of the phosphorescence spectrum is determined by vibronic-spin-orbit coupling [4]. In accordance with it, vibronic transitions with excitation of nonplanar vibrations are the most active in the spectrum, and the 0–0 line and lines of planar totally symmetrical vibrations are faintly visible in the spectrum. At the same time, in the phosphorescence spectrum of 2,3,7,8-TCDD, the lines corresponding to pure electronic transition and totally symmetrical vibrations are the most intense (Fig. 1). In this molecule the lowest triplet is a $B_{1u} \pi 1\pi^*$ state, radiative transition takes place due to spin-orbit coupling and the structure of the spectrum is determined by Franck–Condon electron–vibration interactions.

A spectrum of a mixture of 2,3,7,8-TCDD and 2,4,7,9-TCDD at concentrations of 4.5×10^{-5} and 3×10^{-5} M is presented in Fig. 5. Quasi-lines of the emission spectrum of the binary solution can be unambigu-

Table I. Position of Main Quasi-Line of Dioxin Phosphorescence Spectra at 77 K

Compound	Wavelength (nm)								
Unsubstituted	394	396	400	402	412	420	427	430	441
2-CDD	396	399	402	408	410	414	424	430	
2,3-DCDD	402	406	407	412	416				
2,3,8-TrDD	403	407	408	410	415	418	432		
2,3,7,9-TCDD	406	410	412	417	420	428	434	438	
2,3,8,9-TCDD	406	407	410	417	428	434	439		
2,3,7,8-TCDD	410	412	417	421	433	438	441	447	
2,4,7,9-TCDD	409	411	415	417	419	426	433	437	440
1,2,3,7,8-PeCDD	410	413	415	421	436	442	451		
1,2,3,4,7,8-HCDD	408	415	420	426					
1,2,3,6,7,8-HCDD	414	417	424	440	443	446			
OCDD	419	423	430	436	443	449	454	462	

Fig. 1. Phosphorescence spectrum of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in *n*-hexane at 4.2 K.Fig. 2. Phosphorescence spectrum of 2,4,7,9-tetrachlorodibenzo-*p*-dioxin in *n*-hexane at 4.2 K.Fig. 3. Phosphorescence spectrum of 2,3,8,9-tetrachlorodibenzo-*p*-dioxin in *n*-hexane at 4.2 K.Fig. 4. Phosphorescence spectrum of 2,3,7,9-tetrachlorodibenzo-*p*-dioxin in *n*-hexane at 4.2 K.

ously attributed to a certain component of the mixture. This is an illustrative example of the technique's possibilities for the selective determination of isomers by

such spectra. Phosphorescence spectra of chlorine isomers of dioxin at 77 K are less suitable for the selective

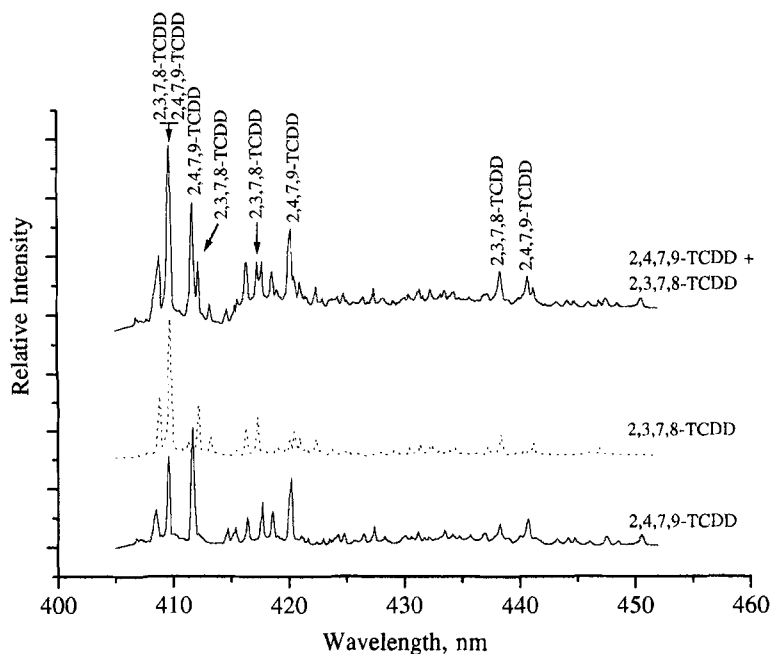


Fig. 5. Phosphorescence spectra of polychlorinated dioxins in *n*-hexane at 4.2 K.

registration, because of the large (2- to 4-nm) line half-widths. But the simplicity of the equipment and the registration process provides the possibility for the development of screening methods for detecting dioxins.

Evaluation of the detection limit for dioxin was performed for our spectral equipment. It was established that a reliable spectrum recording is ensured for concentrations down to 5×10^{-8} M. When analyzing microvolumes of 2,3,7,8-TCDD, we are able to determine its content at a level not exceeding 100 Pg. On lowering the temperature to 4.2 K, the half-widths of vibronic lines decrease, and their peak intensities significantly increase, so the limit of TCDD detection at 4.2 K should be significantly lower.

Thus, in this paper it is demonstrated that phosphorescence spectra of PCDD under conditions of the Shpolskii effect have a well-resolved vibronic structure. The existence of distinctions in the quasi-linear phosphorescence spectra even for close isomers of polychlor-

inated dioxins allows us to hope that it will be possible to detect these compounds reliably in complex mixtures.

ACKNOWLEDGMENTS

The investigation was carried out with the support of the Russian Foundation of Fundamental Research under Grant N 96-03-34089.

REFERENCES

1. A. E. Pohland and G. C. Yang (1972) *J. Agr. Food Chem.* **20**, 1093–1099.
2. J. M. Khasawneh and J. D. Winefordner (1988) *Talanta* **35**, 267–270.
3. V. G. Klimenko, R. N. Nurmukhametov, and A. A. Stehin (1994) *Dokl. Russ. Akad. Nauk* **336**, 489–491.
4. V. G. Klimenko, R. N. Nurmukhametov, and E. A. Gastilovich (1997) *Optika Spectr.* **83**, 92–96.
5. R. N. Nurmukhametov, V. G. Klimenko, I. L. Belaits, and S. A. Lebedev (1996) *Zh. Fiz. Khim.* **71**, 148–151.