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Optical spectra and photophysical properties of polychlorinated dibenzo-*p*-dioxin derivatives

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Abstract. Published data on the optical spectra and theoretical investigations of dioxins, polychlorinated derivatives of dibenzo-*p*-dioxin, which are well-known environmental toxins, are generalised. The geometrical and electronic structures of the molecules and their vibrational and electronically excited states are considered. The influence of the number and positions of chlorine atoms in dioxin molecules on the optical spectra (IR and UV absorption, fluorescence and phosphorescence spectra), in particular, on the low-temperature fine-structure phosphorescence spectra of solid solutions and on the photophysical deactivation of triplet electronic states are discussed. The results of the use of optical spectroscopy for identification and quantification of dioxins are presented. The bibliography includes 108 references.

I. Introduction

Compounds of the dibenzo-*p*-dioxin series, also called dioxins, became widely known and fell into disrepute after high toxicity of some polychlorinated dibenzo-*p*-dioxins (PCDD) had been established.[1–5] Due to their high stability, dioxins formed in industrial processes can be retained in soil and water for long periods, enter living organisms and be accumulated in them. Due to the extreme hazard of dioxin ecotoxicants, investigation of their physicochemical properties and development of highly sensitive methods for their detection and quantification have become urgent.

Several reviews devoted to the methods and results of determination of PCDD in environmental objects and biological tissues have been published;[6–10] however, they mainly discuss the data of GC/MS methods of analysis, while the data of spectroscopic studies used for analytical purposes are scanty. Since the mid-1980s, the physicochemical properties of PCDD have been studied more vigorously, in particular, by spectroscopic methods. These methods possess a great analytical potential; they can be used to identify various PCDD in different media and to perform quantitative analysis. Futhermore, spectroscopic methods can also be used to solve a fundamental problem, namely, to elucidate the relationship between the structures and physicochemical properties of PCDD molecules. They provide valuable information about the interaction of the molecule with light, its steric and electronic structure, various types of intra- and intermolecular interactions, *etc*. With the progress in elucidation of the structure and physicochemical properties of PCDD, the mechanism of toxic action and the pathways of deactivation of these toxins would gradually become clear.

The present review is, in our opinion, the first attempt to survey the published data obtained by both experimental and theoretical methods of optical spectroscopy on the structure, vibrational and electronic states of dioxin molecules and the physicochemical properties of dioxins. Data from IR, Raman, electronic absorption, fluorescence and phosphorescence spectra are discussed, in particular, fine-structure electronic-vibrational (vibronic) phosphorescence spectra at temperatures of 77 and 4.2 K are presented. The manifestation of vibronic and vibronic-spin-orbit couplings in the fine structure of vibronic spectra, the change of the nuclear configuration of molecules in the triplet excited state, the rate constants of radiative deactivation of singlet and triplet electronic states, and the effect of the number and the positions of chlorine atoms in the PCDD molecule on the phosphorescence spectra and the phosphorescence rate constants are discussed. The last Section contains the results of the use of optical spectra (UV and IR absorption, fluorescence, phosphorescence) for identification of dioxins and determination of their quantity.

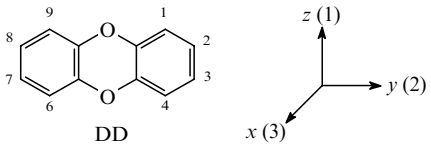
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II. Molecular and electronic structure of dioxins

1. Molecular structure

Dibenzo-*p*-dioxin (DD) is an aromatic cyclic ether consisting of two benzene rings connected through oxygen bridges.



DD

X-Ray diffraction data for DD [11–13] and for five of its chloroderivatives [mono-, di-, tetra-, hexa-, and octachlorodioxins (OCDD) [14–19]] have been described in the literature. In the crystals, the dioxin molecules are nearly planar, although some atoms including Cl atoms deflect from the plane. Thus in di- [16] and

hexachlorodioxin molecules,[17] the angle between the C−Cl bond and the plane amounts to 3–4°, while in mono-,[14,16] octa-[16,18] and tetrachlorodioxins,[15,16,19] this angle does not exceed 2°. The C−Cl bond length in mono-, di- and hexachlorodioxin molecules varies from 1.69 to 1.75 Å. The geometric parameters of the central fragment of the molecules differ insignificantly: the C−O bond length is equal to 1.36–1.38 Å and the angle between the C−O bonds (δ_{COC}) is ~116°. Thus, the size of the COC angle in dioxins is intermediate between those in anisole (110°) and diphenyl oxide (120°).[20]

According to X-ray diffraction data, the central fragment of dioxin molecules can be considered to be planar. In the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (β-TCDD),† the oxygen atoms deflect slightly from the plane through the four carbon atoms in different directions, thus forming a 'chair' configuration of the central fragment.[16] However, the angle of deflection is only 0.8°. In the DD molecule,[11] all six atoms of the central fragment lie in one plane but this plane as a whole is somewhat (by 0.5°) rotated around axis 1. The C−O bond length in dibenzo-*p*-dioxin is 1.383 Å, the internal and external CCO angles are 122° and 118°, and the central COC angle is 116°. Note that the geometric parameters determined from X-ray diffraction data refer to molecules forming the crystal lattice. No experimental data for these parameters in free dioxin molecules have been reported in the literature.

In several studies, the geometric structures of dioxins have been determined theoretically, the geometry being optimised using semiempirical[21] and *ab initio*[22,23] calculations. According to some data,[21,22] the DD and β-TCDD molecules are planar and the calculated values of bond lengths and angles are close to those found experimentally.[15] According to another publication,[23] the DD molecule is non-planar: the benzene rings are rotated with respect to the axis which passes through oxygen atoms (axis *z*) to form a dihedral angle equal to 167.93° (subsequently, this molecular configuration is called a 'butterfly'). According to a calculation[23] carried out in the same approximation, the cation derived from the DD molecule is planar in the ground electronic state.

In an earlier publication,[21] DD has also been suggested to have a 'butterfly' configuration. Thus the dipole moment of a solution of DD in benzene was found to be 0.55 D (rather than zero). The molecule was modelled as the 'butterfly' configuration and the dihedral angle was estimated from the dipole moment. It was found to be 164°. Note that this conclusion cannot be regarded as unambiguous because the molecule could acquire a dipole moment due to interaction with the solvent without losing planarity; for example, it could occur as a configuration with C_{2v} symmetry with retention of the $C_2(z)$ symmetry axis.

The problem of the structure of dioxins attracts attention because the toxicity of PCDD is supposed to be correlated with either planar or non-planar structure of their molecules.[24] Grainger *et al.*[24] proposed determination of the molecular configuration on the basis of the δ_{COC} angle: if this angle is 109–111°, the molecular is non-planar. For some PCDD, the COC angles were found[24] using approximate calculation procedures based on a triatomic model and using spectroscopic data on the frequency of the stretching antisymmetrical vibrations of C−O−C groups. It was concluded that the PCDD molecule becomes more planar as the number of α-chlorine atoms decreases. However, this conclusion should be treated critically because the triatomic model is too rough to provide an adequate description of the vibrations of a polyatomic molecule.

The authors of most spectroscopic studies of dioxins give preference to the planar configuration, relying on the experimental data on molecular geometry; however, some researchers decide in favour of the 'butterfly'.

† In considering the spectral properties of polyaromatic derivatives, for example, substituted naphthalenes, anthracenes, 9,10-anthraquinones and so on, the positions of substituents are designated by Greek letters.

The highest-symmetry group to which planar dioxin molecules can belong is the D_{2h} group (this group of symmetry corresponds to the planar molecules of DD, β-TCDD, 1,4,6,9-Cl_4DD and OCDD). A molecule with the 'butterfly' configuration has C_{2v} symmetry in which the following symmetry elements are retained: the $C_2(x)$ axis and two symmetry planes σ_1 and σ_2, perpendicular to the Cartesian coordinates *z* and *y*, respectively. The $C_{2v}(D_{2h})$ groups of symmetry are matched by the following correlation of irreversible representations:

$$A_1(A_g + B_{3u}),\ B_2(B_{2u} + B_{1g}),\ B_1(B_{1u} + B_{2g}),\ A_2(B_{3g} + A_u). \qquad (1)$$

To answer the question about the configuration of the dioxin molecules mentioned above, it is expedient to use correlation (1) and employ selection rules when analysing spectroscopic data (see Sections III and IV).

2. Electronic structure of molecules

The ground electronic state (S_0) of the planar DD molecule is characterised by the following charges (ρ_e) on the atoms of the central fragment, oxygen and four carbons: $\rho_e(O) \approx -0.37$ and $\rho_e(C) \approx +0.22$ (in the electron charge units) on each of equivalent atoms. The calculation was carried out by the INDO/S semiempirical approximation. The charges on the C−H group atoms are small in magnitude (~0.05–0.09 units) and have opposite signs (for carbon $\rho_e < 0$).

The presence of four Cl atoms in the planar β-TCDD molecule does not change the charge distribution in the central fragment with respect to that in DD. Charge redistribution in β-TCDD takes place on the atoms of the C−Cl groups — the negative charge on each chlorine atom [$\rho_e(Cl) \approx -0.12$] reverses the sign of the charge on the corresponding β-carbon atoms [$\rho_e(C) \approx +0.11$]. The changes in the charge on the C−H group atoms are reduced to a slight increase in their magnitude ρ_e (to ~0.08–0.12), their signs being retained. The same pattern of charge distribution is observed for OCDD: $\rho_e(O) \approx -0.34$, $\rho_e(C) \approx +0.20$ in the central fragment, while for C−Cl groups with the chlorine atoms in the α- and β-positions $\rho_e(Cl) \approx -(0.09-0.10)$ and $\rho_e(C) \approx +(0.07-0.09)$.

Thus, an increase in the number of Cl atoms in dioxin molecules (from zero to eight) barely influences the charge distribution on the atoms of the central six-membered fragment of the molecules in the ground electronic state S_0. A theoretical study[25] of the electron-donating properties of DD, β-TCDD and 1,4,6,9-Cl_4DD molecules has also demonstrated that the π-donor properties of these molecules (as well as their geometric structure) depend only slightly on the positions of Cl atoms.

An important characteristic of the ground electronic state S_0 of a molecule is the ionisation potential (IP). The first IP for several dioxin molecules (DD, 2-ClDD, 2,8-Cl_2DD) cooled in a supersonic jet of argon were determined experimentally by the resonance-enhanced two-colour two-photon ionisation technique.[23,26] For nine dioxins containing zero to eight chlorine atoms in the molecule, a semiempirical calculation[23] of the IP values in the Koopmans approximation was performed. It was found that, as the number of chlorine atoms in the molecule increases, the IP value increases monotonically by approximately 0.1 eV for each additional Cl atom. Indeed, the IP for DD, β-TCDD and OCDD are 7.58, 7.99 and 8.42 eV, respectively. It is of interest that the pattern of dependence of the IP on the number of Cl atoms in dioxins differs substantially from that observed in the series of chloro-substituted benzene derivatives in which the number of Cl atoms ranges from zero to six.[23,27] In the case of chlorobenzenes, the IP value barely changes upon an increase in the number of Cl atoms (9.25 and 9.19 eV for benzene and hexachlorobenzene, respectively). This difference between the patterns of IP variation for these series of compounds was attributed[23] to the presence of oxygen in dioxin molecules.

According to the Koopmans approximation, the IP values are determined by the energy of the highest occupied molecular orbital (with allowance for an adjusting parameter selected

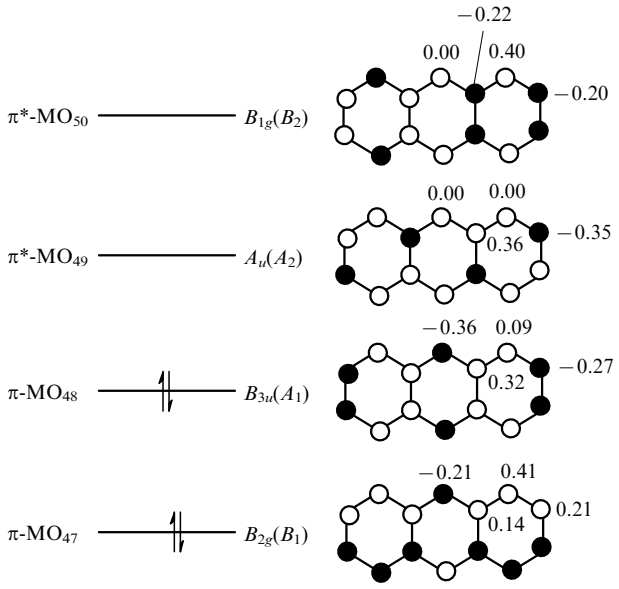


Figure 1. Classification of four MO of the DD molecule according to irreducible representations of the $D_{2h}(C_{2v})$ groups and their representation as a LCAO. The numerical values for the coefficients [28] at the $2p_x$-AO are given; the dark and light circles correspond to different signs of the coefficients at these AO.[23]

empirically for a particular series of molecules, for example, for dioxins [23]). Figure 1 shows a π-MO (MO_{48}) of the DD molecule for which the 'butterfly' configuration has been accepted.[23] From representation of the structure of this MO_{48} as a linear combination of atomic orbitals (AO), one can see that the oxygen atoms can actually affect substantially the IP in the DD molecule.

In connection with the results of studies of the dioxin IP, it is of interest to mention the data obtained in the calculations of the electronic states in the planar dioxin molecules [28, 29] concerning the influence of Cl atoms on the structure of the highest occupied π-MO(B_{3u}), which determines the theoretical IP value. It was found that for this MO, the coefficients at the $2p_x$-AO centered at the O and C atoms in the β-TCDD and OCDD molecules with D_{2h} symmetry differ only slightly (by hundredths of a unit) from the corresponding values for the DD molecule (see MO_{48} in Fig. 1). For OCDD, the coefficients at the $2p_x$-AO of the chlorine atoms proved to be relatively low: +0.13 for β-Cl and −0.03 for α-Cl. Since the coefficients at the $2p_x$-AO of oxygen for MO in DD, β-TCDD and OCDD do not depend (with an accuracy of < 3%) on the number of chlorine atoms in the molecule, in our opinion, the difference between the patterns of variation of IP in chlorobenzenes and dioxins can hardly be definitely attributed to the influence of the O atoms, as has been proposed in a publication.[23]

Figure 1 also shows characteristics of a lower occupied MO_{47}, the removal of an electron from which [23] transforms the DD molecule into a cation, as well as characteristics of the vacant MO_{49} and MO_{50}. The electronic configurations corresponding to the transition of an electron from MO_{48} to MO_{50} and from MO_{47} to MO_{49} determine the properties mainly of the lower singlet electronically excited state S_1 having $B_2(B_{2u})$ symmetry. This is a resonance state in two-photon two-colour resonance-enhanced ionisation experiments.[23] Analysis of the signs of the coefficients at $2p_x$-AO (see Fig. 1) centred on the atoms of the C−O−C groups for four MO led the researchers to the conclusion[23] that the DD molecule has different configurations in different electronic states. For instance, on passing from the S_0 state with a 'butterfly' configuration to the cationic form or to the S_1 state, the DD molecule is believed to become flatter, due to the increase in the bond orders in these states. However, the arguments presented in the study in question [23] seem inconclusive. The spectroscopic data concerning the problem of the configuration of the DD molecule in different electronic states (S_0 and S_1) are presented in Section IV.

III. Vibrational states

1. Experimental data

The molecules of dioxins contain 22 atoms and have 60 normal modes. In planar molecules, 41 modes are in-plane vibrations and 19 modes are out-of-plane vibrations. In the infrared, Raman, fluorescence and phosphorescence spectra, which display the vibrations of molecules in the ground electronic state, only vibrations with particular types of symmetry can be observed, depending on the symmetry of the molecule, in accordance with the selection rules.

In molecules with D_{2h} symmetry, vibrations are classified into eight representations (types of symmetry) of this group:

$$11A_g + 10B_{3g} + 10B_{1u} + 10B_{2u} + 4B_{1g} + 5B_{2g} + 5A_u + 5B_{3u}.$$

The last four types are out-of-plane vibrations (which normally correspond to frequencies of < 1000 cm^{-1}). Vibrations with *g* type of symmetry are active in the Raman spectra, while *u*-type vibrations (except for A_u) are IR active. The vibrations active in the phosphorescence spectra are totally symmetric A_g and non-totally symmetric vibrations of either *g* or *u* type, depending on the type of symmetry of the electronically excited state. Of the set of non-totally symmetric vibrations, out-of-plane vibrations are usually responsible for the most intense lines in the ππ* phosphorescence spectra of heteroaromatic compounds [30] (it is these spectra that are typical of dioxins).

Thus, in order to gain exhaustive information concerning the vibrations of dioxin molecules with a symmetry higher than C_s, various spectroscopic methods should be used. Meanwhile, IR spectra of dioxins have been studied most extensively due to the necessity of identifying these hazardous compounds.

The molecules of chlorinated dioxins contain heavy Cl atoms; the frequencies of the fundamental vibrations of these molecules vary [22] over a broad range, ~3300 – 20 cm^{-1}. However, as a rule, the IR spectra of dioxins are measured [2, 24, 31–37] in a narrower frequency range, namely, above 800 cm^{-1}. Data on the IR vibration frequencies of PCDD molecules in KBr pellets,[2, 31] in the gas phase,[24, 34] and under conditions of matrix isolation (argon matrix at 12 K) [33, 35–37] have been reported. In particular, the spectra of 22 isomers of tetrachloro-substituted DD in an argon matrix and in the vapour phase were recorded.[33]

The attention was focused on the IR spectra of the most toxic β-TCDD.[2, 32–34] The IR spectrum of this compound in a KBr pellet was measured [2] in a wider frequency range (4000 – 375 cm^{-1}) than the spectra of other tetrachloro-substituted DD. Figure 2 shows a fragment of this spectrum.[37]

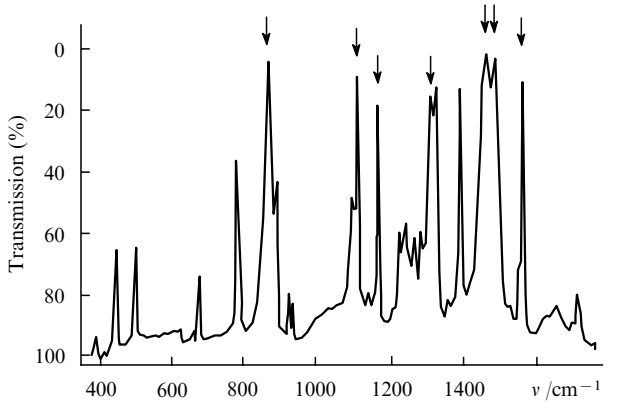


Figure 2. IR absorption spectrum of β-TCDD in a KBr pellet.[2] The arrows mark the spectral regions in which analytical lines were identified in a study with matrix isolation.[37]

The researchers were especially interested in the fact [22, 34] that the IR spectra of tetrachloro-substituted DD recorded under various experimental conditions exhibited doublet splitting of some lines. In the case of β-TCDD, this splitting is observed in the region of 1480, 1315 and 1115 cm^{-1} (see Fig. 2). The results of a theoretical study of the possible causes of this effect in β-TCDD gave rise to the conclusion [22] that Fermi resonance is the main reason.

If the molecular configuration of any dioxin has an inversion centre, only about a half of the fundamental modes are displayed in the IR spectra, while the other frequencies are active in the Raman spectra. The most comprehensive IR and Raman data have been reported for DD [38, 39] and OCDD [40] (Raman spectra of OCDD are shown in Fig. 3). For other PCDD, to the best of our knowledge, no data on the Raman spectra are available.

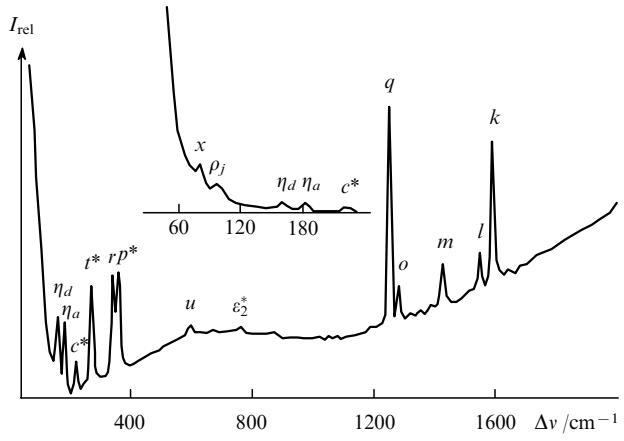


Figure 3. Raman spectrum of the OCDD powder, $\lambda_{excit} = 488$ nm.[40] The spectral lines are marked by the letter designations of vibrations used in Tables 1 and 2. The asterisk marks the vibration frequencies for which a different interpretation is possible (see Table 4).

The frequencies of the fundamental modes of the molecules of some dioxins [DD, β-TCDD, 1,3,6,8-tetrachlorodibenzo-*p*-dioxin (α,β-TCDD), OCDD] in the ground electronic state were also determined by analysis of the fine-structure phosphorescence spectra [39, 41–43] (the results of analysis of these spectra are outlined in Section V). For DD, 2,7-Cl_2DD, 2,8-Cl_2DD and 2,3-Cl_2DD molecules cooled in a supersonic jet, the vibrational structure of the first singlet electronically excited (S_1) state was obtained using the resonance two-photon ionisation method.[23, 26, 44–46]

On the basis of a study of the IR spectra, an empirical interpretation of a number of absorption bands of dioxins has been proposed.[2, 24, 31, 37] As an example, we cite the empirical interpretation of seven frequencies corresponding to the analytical lines in the β-TCDD spectrum (see Fig. 2):[37] 1575, 1489, 1471 cm^{-1} are skeletal in-plane vibrations of the C=C groups in the aromatic fragments; 1312 cm^{-1} is an antisymmetric stretching vibration of the C–O–C groups; 1176 and 1117 cm^{-1} are in-plane deformation and stretching (breathing) vibrations of the aromatic fragments; and 879 cm^{-1} is an out-of-plane vibration of the C–H groups. Studies of the vibrations of dioxins resorting to the data of theoretical calculations [22, 39–41] have shown that this assignment has to be corrected.

2. Calculation and interpretation of vibrations

The calculations for vibrations in the harmonic approximation were performed with the assumption of a planar configuration of the molecule. For several tetrachloro-substituted DD isomers (β-TCDD, 1,4,6,9-Cl_4DD, 1,3,7,8-Cl_4DD, 1,4,7,8-Cl_4DD) [22] and a number of hepta- and hexa-chloro-substituted PCDD isomers,[47] an *ab initio* quantum-chemical calculation of vibrations was performed using scaling factors. For a number of molecules having the same D_{2h} symmetry but different numbers of chlorine atoms, DD, β-TCDD and OCDD, the normal modes were calculated [39–41] by the classical method.[48] When applying this method to dioxins, the potential field of a molecule with a similar structure (xanthone) was chosen as the base.[49, 50] As the hydrogen atoms were replaced by chlorine atoms, the increments [39] corresponding to the force constants of the C–C(Cl)–C groups in chlorinated benzenes were introduced without variations. Scaling factors for some natural vibrational coordinates of related molecules were used in the *ab initio* calculation;[22, 51] for PCDD, they were not varied either.

The results of calculations were used to determine the frequencies of all the normal modes of the dioxins studied;[22, 39–41] an interpretation for each vibration was proposed.

In view of the fact that each vibration of the molecule usually has a complex form (combination of the amplitudes of variation of all bond lengths and bond angles in the molecule), different approaches to the interpretation have been proposed;[50, 51] they were presented, for example, in Refs 22 and 40. One approach [51] makes use of the results of calculations of the distribution of the total energy of vibrations over atomic groups. In this case, each calculated vibration frequency in dioxins [22] is usually matched to vibrations of several atomic groups. For instance, the intense band with a maximum at about 1480 cm^{-1} (see Fig. 2) in the IR spectrum of β-TCDD was assigned [22] to the skeletal vibrations of the aromatic fragments and the deformation vibrations of the CH groups in the plane of the molecule. In another approach,[50] for each calculated normal mode of dioxins,[40] data on the local type of symmetry were taken into account [within the framework of the $D_{6h}(D_{2h})$ groups of symmetry for the movement of atoms in the separate six-membered fragment of the molecule [50]], in addition to the relative vibration amplitudes of separate groups of atoms (Table 1). In Table 1, the vibration modes were assigned to the vibrations of particular atomic groups – the benzene fragment

Table 1. Letter designations [40] of the vibrations of dioxins and their assignment.

Designation of vibrations [a]	Atomic group
In-plane vibrations	
k [$e_{2g}(a_g)$], l [$e_{2g}(b_{3g})$], m [$e_{1u}(b_{1u})$], n [$e_{1u}(b_{2u})$], o [$b_{2u}(b_{2u})$], r [$a_{1g}(a_g)$]	C=C stretching (BF)
p [$b_{1u}(b_{1u})$], s [$e_{2g}(b_{3g})$], t [$e_{2g}(a_g)$]	CCC deformation (BF)
q (a_g), q (b_{2u}), z (b_{3g}), z (b_{1u})	CO stretching (CF)
u (a_g), c (b_{1u}), c (b_{3g})	COC, OCC deformation (CF)
a [$b_{2u}(b_{2u})$], b [$e_{1u}(b_{1u})$], d [$e_{1u}(b_{2u})$], e [$a_{2g}(b_{3g})$]	CCH deformation [b]
ε	CCl stretching
η	CCCl deformation [c]
Out-of-plane (deformation) vibrations	
υ [$b_{2g}(b_{2g})$], y [$e_{2u}(b_{3u})$], ω [$e_{2u}(a_u)$]	CCCC (BF)
f [$e_{2u}(b_{3u})$], g [$a_{2u}(b_{3u})$], i [$e_{1g}(b_{2g})$], j [$b_{2g}(b_{2g})$]	CH [b]
ρ	CCl [c]
χ (b_{2g}), χ (b_{3u})	CCOC (CF)
x (b_{1g}), x (b_{3u}), h (a_u)	BF + CF [d]

Note. BF and CF are the benzene and central fragments.

[a] The local types of symmetry [$\Gamma(\Gamma')$] of the D_{6h} (D_{2h}) point group are given in brackets.

[b] For terminal atomic groups, the designation [$\Gamma(\Gamma')$] has a meaning if all their four atoms in a fragment are identical.

[c] For C–Cl groups, subscripts can be added to the designations η and ρ corresponding to the letter designations for the C–H groups (to provide a more detailed interpretation of vibrations) if the fragment contains four chlorine atoms.

[d] Vibrations of the benzene fragments mutual with respect to one another.

(local symmetry D_{6h}) and the central fragment (local symmetry D_{2h}) and to vibrations of the terminal (C—H and C—Cl) atomic groups. A more detailed interpretation of vibrations according to their form [40] was performed taking into account the definite alternation of the signs of the amplitudes characterising the changes in the bond lengths and angles in the given molecular fragment; this characteristic is reflected in a definite local (for each fragment) type of symmetry of the $D_{6h}(D_{2h})$ point group. This type of analysis of the forms of vibrations makes it possible to distinguish between normal modes assigned roughly to the same atomic groups (for example, to six-membered carbon fragments). This individual form of a normal mode of dioxin was designated by a special letter symbol (in particular, the known Whiffen designations of the vibrations of benzene and monosubstituted benzene derivatives were used).

Tables 2–5 contain the calculated values for all the vibration frequencies [22,40] in the DD, β-TCDD and OCDD molecules distributed over types of symmetry of the D_{2h} point group, together with the corresponding experimental values found from vibrational spectra (IR and Raman) or fine-structure phosphorescence spectra. In the case of β-TCDD, the calculated vibration frequencies determined by different methods [22,40] are in fairly good agreement; however, the use of different methods for the analysis of the forms of vibrations [50,51] precludes a proper comparison of various approaches to the interpretation.

It is worth noting that the approach [50] taking into account the local symmetry of vibrations (unlike that described in Refs 22 and 51) allows correlation of the vibrations of molecules which belong

Table 2. Frequencies of the in-plane vibrations of the DD and PCDD molecules calculated theoretically and obtained experimentally from the Raman and phosphorescence spectra.

Designations of vibrations	ν_{DD} (R) [a]	$\nu_{\beta\text{-TCDD}}$ (phos) [a,b]	$\nu_{\beta\text{-TCDD}}$ [c]	ν_{OCDD} (R) [a]
Vibrations of A_g symmetry				
k	1602 (1621)	1586 (1600)	1595	1566 (1590)
n	1470 (1500)	1449 (1442)	1483	1346
o	1310	1296 (1284)	1296	1281 (1280)
q	1208 (1226)	1222 (1236)	1226	1256 (1250)
a	1152 (1154)	1119 (1100)	1111	
ε_1				898
ε_2		662 (654)	661	733 (754*)
d	1023 (1030)			
r	735 (726)	745 (739)	741	325 (345)
t	613 (564)	232 (206)	254	242 (274*)
u	363 (398)	586 (548)	555	601 (594)
η_d		167 (149)	183	146 (162)
η_a				169 (181)
Vibrations of B_{3g} symmetry				
l	1610 (1586)	1596	1574	1578 (1550)
m	1452	1380	1358	1392 (1425)
z	1317	1209	1154	1218
e	1254 (1192)	1263	1218	
b	1112 (1094)			
ε_3				730
ε_4		972 (985)	986	974
p	883 (898*)	595	538	324 (358*)
s	547 (534)	637 (628*)	642	525
c	477 (450*)	236	227	198 (220*)
η_b		383 (383*)	391	162
η_e				786

Note. From here on, vibration frequencies are given in cm^{-1}; experimental vibration frequencies determined from Raman (R) or IR and phosphorescence (phos) spectra are given in parentheses. The asterisks mark the unambiguous assignments of frequencies to in-plane or out-of-plane vibrations. The Table does not contain the stretching vibrations of the C—H groups. The pairs of designations ε_1, ε_2 or ε_3, ε_4 imply different signs of the amplitudes of the changes in the C—Cl bond lengths in each BF.
[a] From the data of Ref. 40. [b] From the data of Ref. 39. [c] From the data of Ref. 22.

Table 3. Frequencies of the in-plane vibrations of DD and PCDD molecules calculated theoretically and found experimentally from IR spectra.

Designations of vibrations	ν_{DD} [a]	$\nu_{\beta\text{-TCDD}}$ [a,b]	$\nu_{\beta\text{-TCDD}}$ [c]	ν_{OCDD} [a]
Vibrations of B_{2u} symmetry				
k	1584 (1590)	1564 (1568)	1557	1543 (1550)
n	1466 (1495)	1446 (1456)	1470	1366 (1390)
o	1279 (1300)	1271 (1312)	1269	1256 (1298)
q	1293 (1395)	1290 (1326)	1303	1279 (1320)
a	1151 (1154)			
ε_1				813 (840)
ε_2		1106 (1114)	1107	979 (987)
d	1023 (1030)	864 (876)	870	
r	827 (830)	432 (450)	445	452
t	598 (610)	680 (680)	686	308
η_d				203
η_a		177	198	168
Vibrations of B_{1u} symmetry				
l	1622 (1628)	1610	1629	1594
m	1457 (1462)	1345 (1393)	1387	1388 (1423)
z	1196 (1200)	1186 (1172)	1170	1194 (1196)
e	1327 (1305)	1267 (1242)	1234	
b	1147 (1120)			
ε_3		914 (876)	930	864 (850)
ε_4				996 (1003)
p	883 (854)	834 (789)	786	443
s	676	303	326	332
c	245	119	111	83
η_b		512 (500*)	497	178
η_e				699 (666)

[a] According to Ref. 40. [b] According to Ref. 39. [c] According to Ref. 22.

Table 4. Frequencies of the out-of-plane vibrations of DD and PCDD molecules calculated theoretically and found experimentally from Raman or phosphorescence spectra.

Designations of vibrations	ν_{DD} (R) [a]	$\nu_{\beta\text{-TCDD}}$ (phos) [a,b]	$\nu_{\beta\text{-TCDD}}$ [c]	ν_{OCDD} (R) [a]
Vibrations of B_{2g} symmetry				
j	977	890	846	
i	861 (898*)			
ρ_i		115	110	358
ρ_j				85 (97)
χ	533	600 (628*)	610	601
υ	725 (748)	730	648	754 (754*)
ω	258 (278)	309	277	199 (220*)
Vibrations of B_{1g} symmetry				
f	943	895 (867)	874	
g	744 (764)			
ρ_g		322 (383*)	372	140
ρ_f				323 (274*)
y	430 (450*)	435 (441)	437	570
x	223 (242)	119	134	67 (80)

[a] According to Ref. 40. [b] According to Ref. 39. [c] According to Ref. 22.

Table 5.Frequencies of the out-of-plane vibrations of DD and PCDD molecules calculated theoretically and found experimentally from IR spectra.

Designations of vibrations	ν_{DD} [a]	$\nu_{\beta\text{-TCDD}}$ [a, b]	$\nu_{\beta\text{-TCDD}}$ [c]	ν_{OCDD} [a]
Vibrations of A_u symmetry				
j	977	891	845	
i	861			
ρ_i		228	216	334
ρ_j				91
υ	741	744	629	767
ω	521	599	610	602
h	144	55	48	38
Vibrations of B_{3u} symmetry				
f	945 (922)	899 (890)	875	
g	750 (743)			
ρ_g		205	168	89
ρ_f				213
χ	511 (450)	515 (500*)	444	606
y	357	403 (390)	383	449
x	70	33	19	31

[a] According to Ref. 40. [b] According to Ref. 39. [c] According to Ref. 22.

to different point groups of symmetry. For example, this approach was used to perform a correlation of all the vibrations in mono-, di- and tetrachloro-substituted 9,10-anthraquinones.[52] In addition, in experimental and theoretical studies of the vibrations of the DD and β-TCDD molecules as well as 9,10-anthraquinone and tetra-β-chloro-substituted 9,10-anthraquinone molecules, it has been established that the frequencies and forms of vibrations for these molecules are very close.[39] Therefore, interpretation of the vibrations of chlorinated 9,10-anthraquinones, which are more readily available, can be taken as the base for the investigation of the corresponding dioxins.[52]

The variation of frequencies of all 60 vibrations following an increase in the number of Cl atoms in the series of DD, β-TCDD and OCDD, the molecules of which correspond to the same group of symmetry D_{2h}, was discussed in detail.[40] We shall briefly note some regularities[40] of the variation of the frequencies of vibrations with the same form in the DD, β-TCDD and OCDD molecules.

In-plane vibrations. The high-frequency in-plane vibrations of the carbon skeleton (in the range of 1650 – 1200 cm^{-1}), which can be assigned to the k, l, m, n, o stretching modes (of the benzene fragments) and q, z stretching modes (of the central fragment), change insignificantly, on the average by 5%, as the H atoms are replaced by Cl atoms (see Tables 2, 3). In the case of the two other stretching vibrations (A_g and B_{2u}) of the benzene fragments, designated by r (which should be matched to the only totally symmetric vibration r of the core of benzene molecule in the region of 995 cm^{-1}), the vibration frequencies found for DD and OCDD differ appreciably, by a factor of about two. Note that the vibrations r are characterised by low frequencies also in other molecules with benzene side fragments, even when they contain no heavy atoms.[50] For example,[53] in anthracene ν_r = 753 (A_g) and 808 cm^{-1} (B_{2u}).

The frequencies of all [except for one, $s(B_{3g})$] low-frequency deformation vibrations of the carbon skeleton of the molecule (p, s, t, c, u) also change substantially, by approximately 200 – 300 cm^{-1} (by up to 65%), when all the H atoms have been replaced by Cl atoms. The stretching vibrations of the C – Cl (ε) groups of the OCDD molecule were matched to frequencies in the region of 1000 – 750 cm^{-1}.

In many studies, considerable attention is devoted to the identification of the IR bands caused by the presence of the C – O ether groups in the molecules.[20] For example, in the case of diphenyl oxide, which contains a C – O – C group, the frequency ν^{as}_{C-O} = 1236 cm^{-1} was assigned to antisymmetric stretching vibrations of this group. In molecules with D_{2h} symmetry, the $q(B_{2u})$ and $z(B_{3g})$ modes can be matched to these vibrations (see Tables 2, 3). In various PCDD, frequencies in the region of 1330 – 1280 cm^{-1} were attributed to an antisymmetric vibration. It is noteworthy that the vibration frequencies of the C – C groups in the anthracene molecule with the rigid six-membered central fragment are close to the vibration frequencies of the C – O ether groups in DD. The frequencies (in cm^{-1}) of the stretching vibrations of the C – O or C – C groups of the central fragment of DD, 9,10-anthraquinone and anthracene are presented below for comparison.[50, 53]

	DD	9,10-Anthraquinone	Anthracene
A_g	1226	1148	1260
B_{3g}	1317	1284	1376
B_{1u}	1200	1335	1274
B_{2u}	1395	1173	1398

In the DD molecule, as in other molecules having a similar structure and containing eight H atoms in the benzene fragments, each of the eight in-plane deformation vibrations of the C – C – H groups belongs to a particular frequency region (see Tables 2, 3), namely, 1360 – 1240 cm^{-1} (e are high-frequency vibrations) and 1150 – 1000 cm^{-1} (a, b, d is a group of relatively low-frequency vibrations). For similar deformation vibrations of the C – C – Cl (η) groups of the OCDD molecule, two appreciably different frequency regions can also be distinguished. The range of 800 – 700 cm^{-1} is typical of the analogues of the vibrations e, while 200 – 150 cm^{-1} is the range where the analogues of the vibrations a, b and d show themselves.

The empirical interpretation of the spectrum does not always coincide with the interpretation based on calculations. Below we present the assignment of vibrations according to their form based on the use of the local types of symmetry for several vibration frequencies of the β-TCDD molecule, which differs from the empirical assignment (presented at the end of Section III.1).[37] Thus the frequency of 1312 cm^{-1} (B_{2u}) refers to the vibration o of the benzene fragments (with the local type of symmetry b_{2u}); 1172 (B_{1u}) and 1114 cm^{-1} (B_{2u}) correspond to the stretching vibrations z of the central fragment and ε of the C – Cl groups, respectively. A frequency of 450 cm^{-1} was assigned to the 'breathing vibration' r of the benzene molecules (the vibration B_{2u} with the local symmetry a_{1g}), while a frequency of 1326 cm^{-1} was attributed to the antisymmetric vibration of the C – O – C groups.

Out-of-plane vibrations. The main distinctive feature of most of the 11 out-of-plane vibrations of the carbon skeleton of the DD, β-TCDD and OCDD molecules is that their frequencies increase rather than decrease upon an increase in the number of Cl atoms in the molecule (see Tables 4, 5). Indeed, in the region above 300 cm^{-1}, the frequencies of only two, the highest-frequency out-of-plane vibrations of OCDD (of the υ type, assigned to the benzene fragments) change relatively slightly (by 3% – 4%) with respect to the frequencies of the same vibrations in β-TCDD and DD. The other vibration frequencies increase appreciably, by 13% – 33%, which implies displacement of the bands in the spectrum by 70 – 140 cm^{-1}.

A different pattern of variation is observed for the other four lower-frequency vibrations of the molecular skeleton (below 300 cm^{-1}), namely, one vibration ω, which was assigned to the benzene moieties, and three vibrations x and h, assigned to the central moiety. These frequencies, conversely, tend to decrease (by 25% to 75%).

It should be mentioned that the vibrations x and h can be related to the rotations of two benzene fragments with respect to one another (Fig. 4). The molecule thus assumes a 'butterfly' (x, B_{3u}), 'chair' (x, B_{1g}) or 'propeller' (h, A_u) configuration. For comparison, Fig. 4 shows the form of the high-frequency out-of-

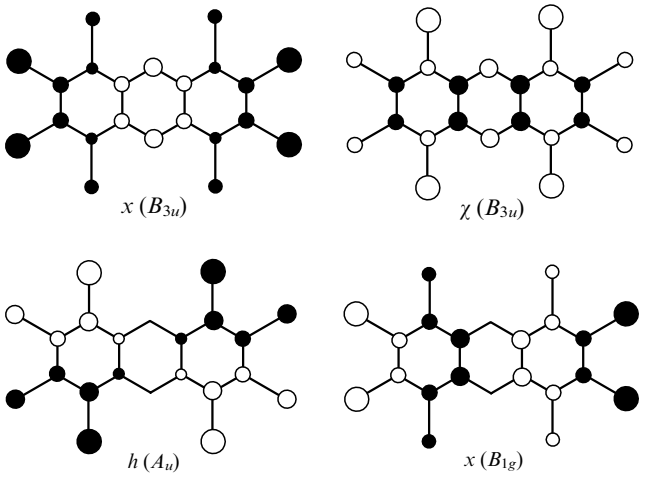


Figure 4. Forms of some out-of-plane vibrations of the DD molecule of D_{2h} symmetry (for vibration frequencies, see Tables 4, 5). The signs and the magnitudes of the displacements of atoms with respect to the plane of the molecule are marked by circles of different sizes and colours.

plane vibration χ (B_{3u}). It can be seen that both x and χ vibrations of the B_{3u} type can be attributed to the molecule in the 'butterfly' configuration but x is related to a larger extent to the rotations of the benzene fragments and χ is related to the shifts of oxygen atoms.

The four out-of-plane vibrations of the C–Cl groups (ρ) of the β-TCDD molecule show themselves at low frequencies, about $\sim$100, 215 and 320 cm^{-1}. An increase in the number of chlorine atoms does not result in any significant increase in the frequency range for the eight vibrations ρ of the OCDD molecule; these vibrations remain in approximately the same frequency regions: $\sim$90–140, $\sim$215 and $\sim$360 cm^{-1}.

Note that the eight out-of-plane vibrations of the C–C–H groups in DD, like those in other molecules having a similar structure and containing eight H atoms in the benzene fragments, correspond to a definite frequency region: 980–940 cm^{-1} (*j, f*), $\sim$860 cm^{-1} (*i*), 750–680 cm^{-1} (*g*). However, it was found that similar vibrations of the C–C–Cl groups (ρ with the corresponding subscripts) of the OCDD molecule cannot be matched successively to higher or lower frequencies (see Tables 4, 5). For example, both ρ_j and ρ_g vibrations in OCDD are characterised by low frequencies.

Molecular configuration. To decide between the planar and non-planar ('butterfly') configurations of the DD and OCDD molecules, we shall consider the structure of their Raman spectra taking into account the selection rules for the D_{2h} and C_{2v} groups of symmetry and the correlation of their irreducible representations (1). If the molecule has the 'butterfly' configuration, *i.e.* belongs to the C_{2v} symmetry group, all the vibrations should be active in the Raman spectra, including the *u*-type vibrations, which are forbidden in the case of the D_{2h} group [see expression (1)]. In particular, the out-of-plane B_{3u} vibrations of the D_{2h} group become totally symmetric. The results of interpretation of the Raman spectra of two dioxins, DD and OCDD, demonstrate that all lines in the spectra of these compounds can be assigned to *g*-type vibrations, which implies a planar configuration of the molecule (see Fig. 3, Tables 2, 4).

IV. Singlet electronically excited states

1. Experimental data

Dioxins, like most benzene derivatives, are colourless, *i.e.* they do not absorb light in the visible region. The UV absorption spectra of dioxins [$S_m(\pi\pi^*) \leftarrow S_0$] have been studied in solution [2, 54–57] and in the vapour phase.[58] Tables listing the absorption maxima and the molar extinction coefficients (ε_{max}) have been reported;[2] the absorption curves for DD and its chloro-derivatives (β-TCDD, 1,2,3,7,8-Cl_5DD and OCDD) can be found in several publications.[55, 56, 58]

The absorption spectra of DD and PCDD occur in the region of 200–350 nm and consist of two bands — a weak broad long-wavelength band (**A**) in the region of 280–320 nm with a maximum at $\sim$300–304 nm and a short-wavelength narrow intense band (**B**) with a maximum at about $\sim$220–240 nm. It can be seen from the absorption curves of some dioxins [56, 58] that the high-frequency absorption band has one more, even shorter-wavelength maximum (**C**); for example, in the spectra of solutions of DD, it is separated from band **B** by $\sim$5.5 nm.[55] As examples, Figs 5 and 6 show the absorption spectra of a solution of DD and of the β-TCDD vapour.

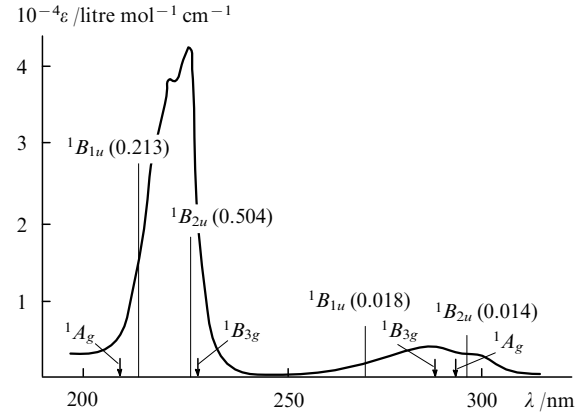


Figure 5. Electronic absorption spectrum of a solution of DD in isopentane at 77 K [56] and results of a quantum-chemical calculation [29] (vertical lines) of the energy and the type of symmetry of electronic ππ* states and the oscillator strengths of transitions (given in parentheses). Dipole-inactive transitions are marked by arrows. The calculated spectrum as a whole is shifted by $\sim$5000 cm^{-1} to lower frequencies.

The ratio of the molar extinction coefficients of bands **B** and **A**, $\varepsilon_{\mathbf{B}}/\varepsilon_{\mathbf{A}}$, for solutions of DD in isopentane [56] is equal to $\sim$10, while for β-TCDD and OCDD vapours,[58] $\varepsilon_{\mathbf{B}}/\varepsilon_{\mathbf{A}} = 9$ and 35. In particular,[58] for OCDD, $\varepsilon_{\mathbf{A}} = 0.05 \times 10^4$ and $\varepsilon_{\mathbf{B}} = 1.73 \times 10^4$ litre mol^{-1} cm^{-1}.

It should be noted that the data on the molar extinction coefficients are presented in few publications and, moreover, the reported ε values are not always close in magnitude. For example, for DD in isopentane,[57] chloroform [2] and heptane,[21] $\varepsilon_{\mathbf{A}} = 0.37 \times 10^4$, 0.37×10^4 and 0.74×10^4 litre mol^{-1} cm^{-1}; for β-TCDD in chloroform [2] and in the vapour phase,[58] $\varepsilon_{\mathbf{A}} = 0.56$ and 0.41×10^4 litre mol^{-1} cm^{-1}. The $\varepsilon_{\mathbf{A}}$ values reported for vapour and for chloroform solutions of OCDD [2, 58] differ by a factor of five. These differences may be due to both the interaction of dioxins with a solvent and the error in the determination of the true concentration of dioxins in the samples studied.

The spectra of chloroform solutions of DD and several PCDD [2] showed an unusual intensity ratio of the absorption bands, namely, the short-wavelength band **B** was found to be less intense than band **A**. For example, $\varepsilon_{\mathbf{B}}/\varepsilon_{\mathbf{A}} = 0.28$, 0.53 and 5.5 for DD, β-TCDD and OCDD [for comparison, for DD in isopentane, $\varepsilon_{\mathbf{B}}/\varepsilon_{\mathbf{A}} \approx 10$ (see Ref. 56)]. In our opinion, this effect is caused by the disturbing influence of the solvent, which also absorbs in the short-wavelength region of the spectrum (< 240 nm).[59]

The absorption properties of DD are similar to those of other aromatic ethers. The spectra of ethers usually contain two absorption bands; the long-wavelength band with $\varepsilon \approx (0.16–0.3) \times 10^4$ litre mol^{-1} cm^{-1} is located at about

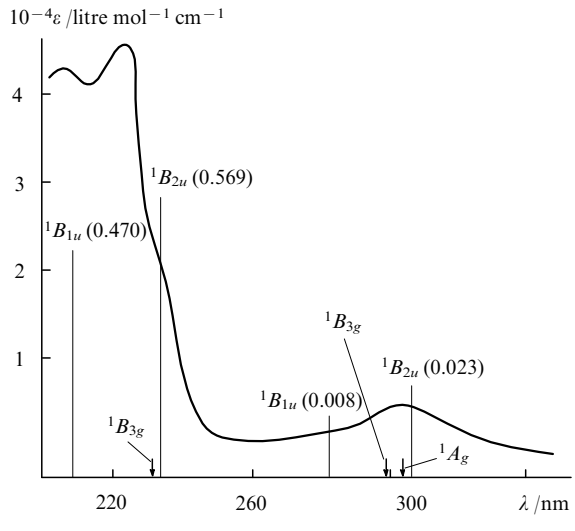


Figure 6. Electronic absorption spectrum of β-TCDD vapours [58] and the results of a quantum-chemical calculation [29] of the energy and type of symmetry of electronic ππ* states and the oscillator strengths of transitions. For designations, see Fig. 5.

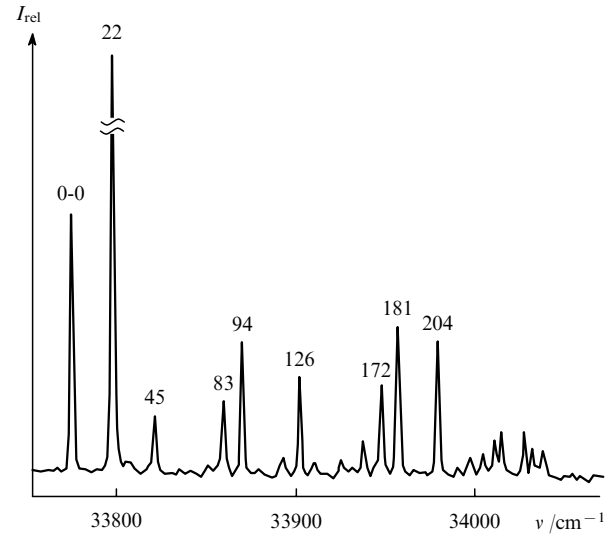


Figure 7. Vibrational structure of the electronically excited state S_1 (ππ*) of DD molecules cooled in a supersonic jet of argon recorded using resonance-enhanced two-photon ionisation.[23]

250 – 290 nm and the short-wavelength band with $\varepsilon \approx (0.8-1.8)\times 10^4$ litre mol^{-1} cm^{-1} occurs in the region of 210 – 240 nm.[20] Both bands are associated with transitions from the electronic states corresponding to the benzene chromophore perturbed by the heteroatom of the ether group.

As the number of chlorine atoms in dioxin molecules increases from zero to eight, the long-wavelength band in the absorption spectra of solutions shifts bathochromically.[2] Thus in the spectra of chloroform solutions of DD, β-TCDD and OCDD, bands **A** are responsible for maxima at 293, 310 and 318 nm. However, in the case of vapours, the positions of the maxima of bands **A** and **B** virtually do not change — in the series β-TCDD, 1,2,3,7,8-Cl_5DD and OCDD, band **A** has a maximum at about 303 – 305 nm, while the maximum of band **B** is at ~223 nm.[58]

In the UV absorption spectra of DD in isopentane recorded at 77 K, the long-wavelength band has several maxima,[56] which can be attributed to the vibrational structure. The vibrational fine structure of the electronically excited state S_1 for the DD, 2,7-Cl_2DD, 2,8-Cl_2DD and β-TCDD molecules was obtained using the method of resonance-enhanced two-photon ionisation in a supersonic argon jet.[44–46] The vibrational structure of the S_1 state of the DD molecule [23] is shown in Fig. 7. In this type of spectrum of any dioxin, the first (lowest-frequency) line was assigned to the purely electronic transition $S_1 \leftarrow S_0$. As a result, the following energies of the S_1 state were determined for these dioxins:[23] 33774 (DD), 32805 (2,7-Cl_2DD), 32729 (2,8-Cl_2DD) and 32100 cm^{-1} (β-TCDD). These frequencies are shifted by ~750 cm^{-1} to shorter wavelengths [23] with respect to those in the spectra of isooctane solutions.

The fine structure of the spectra of the $S_1 \leftarrow S_0$ electronic transition has not been interpreted yet. It should be noted that the results of full interpretation of the spectra performed for many other molecules are widely used, for example, to determine the symmetry of the first electronically excited state, to study the mechanisms of intramolecular interactions, to decide between the retention and the change of the symmetry of the nuclear configuration of the molecule upon transition from the ground state to the electronically excited state and to gain quantitative data concerning the change in the geometrical parameters of the molecule in the electronically excited state. Some results of the interpretation of the spectra of dioxins for the lower triplet state are presented in Section V.

The spectrum shown in Fig. 7 has prompted several conclusions [23] (which we consider erroneous) concerning the nuclear configurations of this molecule in the ground and in the S_1 electronic states. For example, the most intense line of this spectrum (vibration frequency 22 cm^{-1}) was assigned [23] to a 'butterfly' type vibration in the electronically excited state S_1 [the form and the frequency of this vibration, $x(B_{3u})$, in the ground electronic state are presented in Fig. 4 and in Tables 4, 5). Since this spectrum contained numerous low-frequency lines and the researchers found it to be similar to the corresponding spectrum of dihydroanthracene,[60] they [23] arrived at the conclusion that the configurations of the DD molecule in the S_1 and S_0 states are different. It was concluded that the molecule has a 'butterfly' configuration in the S_0 state and becomes flatter in the S_1 state. However, this conclusion appears doubtful. Indeed, the ratio of the intensities of the strong and weak lines in the spectrum of DD (see Fig. 7) can be distorted due to the known saturation effect.[61] In addition, the strong line, assigned to a 'butterfly' type vibration, does not form an intense progression (unlike that in the spectrum of the dihydroanthracene molecule): the lines corresponding to the frequencies 22×2, 22×3, *etc.*, are either weak or missing. Meanwhile, it is intense lines due to vibration overtones in the electronic-vibrational spectra that normally point to a change in the nuclear configuration of the molecule.[62, 63]

2. Calculation of the electronic states

In order to interpret the observed electronic spectra of several dioxins (DD, β-TCDD, α,β-TCDD and OCDD), semiempirical calculations for electronically excited states have been carried out in the PPP, CNDO/S and INDO/S approximations taking into account singly excited electronic configurations.[21, 29, 43, 56, 64, 65] The calculated spectra of DD and β-TCDD, in comparison with the experimental spectra, are presented in Figs 5 and 6. It can be seen that, although the absolute magnitudes of energies in the calculated spectra usually prove to be overestimated, the calculations represent satisfactorily the general pattern of the absorption spectrum, *i.e.* the relative arrangement and the relative intensities of the weak and strong bands.

According to calculations,[29, 43, 65] the spectral region corresponding to the long-wavelength band **A** contains the frequencies of the first four electronic transitions from S_0 to ππ* states, namely, B_{3g}, B_{2u}, A_g and B_{1u} but only two of these states are dipole-active. Note that the mutual arrangement of the energy levels corresponding to the first three electronic states changes

depending on the parametrisation accepted in the semiempirical calculations; thus, the S_1 state can belong to the B_{3g}, B_{2u} and A_g types. To the best of our knowledge, no experimental data on the type of symmetry of the S_1 state are available. The S_4 state in dioxins has B_{1u} symmetry.

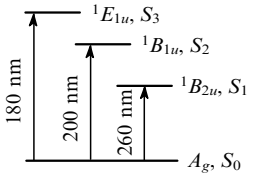
The short-wavelength absorption bands **B** and **C** are due to the third and fourth dipole-allowed transitions from ππ* states with the B_{2u} and B_{1u} types of symmetry, respectively (see Figs 5, 6).

The calculations of electronic states showed that the structure of the ππ*-absorption spectrum indicated above does not change substantially in the sequence DD, β-TCDD, α,β-TCDD and OCDD; the increase in the number of chlorine atoms in the molecule changes somewhat the energies of these states (this is in agreement with the experimental results pointing to the small difference between the positions of the band maxima in the UV spectra of various dioxins). The slight influence of the increase in the number of chlorine atoms on the ππ*-absorption spectrum is also known for other molecules (for example, for chlorinated 9,10-anthraquinones [66]).

It should be mentioned that the calculation, which describes satisfactorily the relative oscillator strengths for transitions, reproduces poorly, as a rule, their absolute magnitudes. For example, according to experimental data ($\varepsilon_{\mathbf{A}} = 0.37 \times 10^4$ litre $mol^{-1}\,cm^{-1}$), band **A** of the DD molecule corresponds to the oscillator strength $f_{\mathbf{A}} = 0.067$.[29] Various semiempirical calculations which used different molecular models and different approximations or parametrisations gave the following $f_{\mathbf{A}}$ values for DD corresponding to the sum of the oscillator strengths of the first two dipole-active transitions: $f_{\mathbf{A}} = 0.368$,[21] 0.032 [29] and 0.17.[64, 65] The calculated [64, 65] relative $f_{\mathbf{B}}/f_{\mathbf{A}}$ values for the DD, β-TCDD and OCDD molecules ($f_{\mathbf{B}}/f_{\mathbf{A}} = 9.8$, 6.2 and 70, respectively) agree in order of magnitude with the ratios of extinction coefficients found experimentally (10, 9 and 35, respectively [56, 58]). Thus, the calculation of the electronic states for planar models of the molecules confirms the experimental data [56, 58] concerning the substantial decrease in the absorption cross-section at 305 nm for OCDD molecule relative to the DD or β-TCDD molecules.

The **A**–**C** bands in the singlet–singlet ππ*-absorption spectrum of DD (or other dioxins) can be matched to the corresponding bands in the benzene spectrum. Scheme 1 shows three transitions from states with different types of symmetry and the corresponding absorption maxima for benzene.[67]

Scheme 1



The $B_{2u} \leftarrow S_0$ and $B_{1u} \leftarrow S_0$ transitions are dipole-inactive in the D_{6h} symmetry group and are allowed only upon vibronic (Herzberg–Teller) coupling.

The B_{1u} and B_{2u} states of benzene should be matched to four states of the DD molecule with D_{2h} symmetry, which contains two benzene fragments, namely, B_{2u} and A_g (analogues of B_{2u} in benzene) and B_{1u} and B_{3g} (analogues of B_{1u} in benzene). In the D_{2h} symmetry group, the B_{2u} and B_{1u} states are dipole-active but (in line with their origin) they are characterised by low oscillator strengths. These four transitions correspond to one weak, the longest-wavelength band **A** in dioxins (see Figs 5, 6).

The band with a maximum at 180 nm in the spectrum of benzene is due to the dipole-active $E_{1u} \leftarrow S_0$ transition. In molecules with D_{2h} symmetry, for example in DD, two (according to the number of benzene fragments) electronic states E_{1u} of benzene are matched by the B_{2u}, B_{1u}, A_g and B_{3g} states. The *u*-type states (B_{2u} and B_{1u}) in DD and in other dioxins should be identified with intense absorption bands **B** and **C** with maxima at about ~250 nm. According to calculations, they are characterised by great oscillator strengths of transitions.

The analogy between the electronic states of benzene and dioxins is confirmed by calculations of the corresponding π-MO of the molecule.[28] Indeed, for at least six lower electronic states, the symmetry of the π-MO of benzene is approximately retained in the benzene fragments of DD. This is reflected, for example, in Fig. 1, which shows the distribution of the coefficients at the $2p_x$-AO centred on the atoms of the six-membered benzene fragments of the molecule for four MO. It can be seen that this distribution is similar to the known distribution of the coefficients in the vacant (E_{1g}) and occupied (E_{2u}) π-MO of benzene.

The oxygen atoms have little influence on the local symmetry of the MO under study, although the lone electron pairs (*l*-electrons) of oxygen, which occupy the $2p_x$-AO, also contribute to π-conjugation (when this is allowed by the type of symmetry of the whole MO of the molecule). They bring about the greatest perturbation of occupied rather than of vacant MO of dioxins.[28, 56] For the highest occupied MO of the DD molecule, this contribution is 26%; in the S_1 state, 0.15 of an electron charge is transferred from the oxygen atoms to the carbon atoms of the benzene fragments.

The effect of *l*-electrons on the S_1 state normally shows itself as a substantial decrease in the energy of the π*l*π* state with respect to the ππ* state and as an increase in the corresponding dipole moment of the transition. For dioxins, this influence of the *l*-electrons of oxygen and chlorine on the S_1 state is slight; hence, the π*l*π* state can be designated by ππ*.

In dioxins, the lone electron pairs (*n* electrons), which occupy $2p_z$- or $2p_y$-AO, form very deeply located MO and the absorption bands corresponding to the $n\pi^* \leftarrow S_0$ transitions should occur in the vacuum UV region. According to calculations,[65] the spectral region between absorption bands **A** and **B** of dioxins, as in the case of benzene, contains bands corresponding to the $\pi\sigma^* \leftarrow S_0$ transitions.

The analogy between the electronic transitions in DD and benzene (with allowance for the slight influence of chlorine atoms on the spectrum) accounts for the distribution of band intensity in the UV spectra of dioxins.

The same analogy can be drawn between the ππ* electronic states of benzene, DD and other molecules, for example, 9,10-anthraquinone and anthracene, which contain, like DD, two benzene side fragments. The DD, 9,10-anthraquinone and anthracene molecule differ in the central fragments. Comparison of the spectral and theoretical data concerning their ππ* states demonstrates the influence of the electronic structure of the central fragment on the mutual arrangement of the first four energy levels. Recall that the first four electronic transitions in DD are responsible for one band **A**. According to theoretical and experimental data,[68] in 9,10-anthraquinone, the energy level of the state analogous to the $S_4(B_{1u})$ state of DD proves to be shifted to short-wavelength region with respect to the first states B_{2u}, B_{3g} and A_g to such an extent that a separate band with a maximum at ~270 nm is attributed to the corresponding transition. Conversely, in the anthracene molecule, the energy level of the state analogous to $S_4(B_{1u})$ in DD is shifted to longer wavelengths with respect to the other three states; thus, it becomes the $S_1(B_{1u})$ state and the onset of the band corresponds to a wavelength of ~280 nm.[53, 69]

Let us briefly summarise the data on the singlet–singlet transitions in dioxins. The long-wavelength band in the absorption spectrum has a combination structure in the sense that it 'hides' transitions from the four electronic states having different types of symmetry: B_{1u}, B_{3g}, A_g and B_{2u}, where B_{1u} corresponds to the S_4 state. Variation of the number of chlorine atoms from zero (DD) to eight (OCDD) does not change generally this structure of the band but results in a nearly parallel shift of the energy levels of the corresponding states towards lower frequencies. The mutual arrangement of the energy levels of the B_{1u} and B_{2u} states changes substantially only in a series of molecules having similar structures but containing different atomic groups in the central fragment, for example, in the series of DD, 9,10-anthraquinone and anthracene, in which the above-mentioned states are of the same nature. Thus,

the structure of the long-wavelength band in the spectra of dioxins is determined by the presence of the ether C–O–C groups in the central fragment.

The energy levels calculated for the B_{2u}, B_{3g} and A_g states in dioxins are close; therefore, additional investigations are required to determine the type of symmetry of the S_1 state of a particular molecule. For example, it would be useful to obtain and study the fine vibrational structure of the fluorescence spectrum.

The low intensity of the long-wavelength band in the spectra of dioxins is due to its origin: the electronic transitions corresponding to this band are analogues of the first two, dipole-inactive transitions in benzene. The change in the number of chlorine atoms generally has little influence on the intensity distribution in the UV spectra of dioxins.

V. Luminescence

Dioxins belong to the class of luminescing compounds. Luminescence is due to the $S_1 \rightarrow S_0$ transition from the lower singlet electronically excited state (fluorescence) and to the $T_1 \rightarrow S_0$ transition from the lower triplet state (phosphorescence). Solutions of dioxins fluoresce in the region of 310–400 nm; when frozen (77 K), they display a bright long-living blue to light-blue phosphorescence. As an example, Fig. 8 presents the emission spectrum of a solution of DD in isopentane recorded at 77 K.[56] This spectrum demonstrates an important feature characteristic of both DD and PCDD, namely, very low intensity of the fluorescence band *1* with respect to the phosphorescence band *2*.

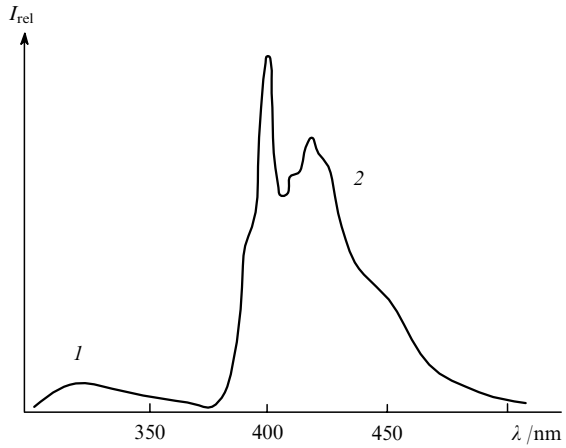


Figure 8. Luminescence spectra of a solution of DD in isopentane at 77 K;[56] (*1*) fluorescence, (*2*) phosphorescence.

1. Photophysical characteristics of luminescence

In this Section, the quantitative data on the deactivation of the first singlet and triplet electronically excited states of dioxins are presented. We discuss experimental values for the quantum yields and the decay times of fluorescence (ϕ_{fl} and τ_{fl}) and phosphorescence (ϕ_{ph} and τ_{ph}), the rate constants for deactivation of the lower singlet and triplet electronically excited states (k_{fl} and k_{ph}), theoretical estimates of the k_{ph} values, and the results of calculations of the influence of the number of chlorine atoms in the molecule on k_{ph} and τ_{ph}.

a. Fluorescence

The fluorescence spectra of solutions of DD and PCDD exhibit a structureless band (see Fig. 8). The use of selective laser excitation of fluorescence, which often gives rise to a fine (vibrational) structure in the spectra of solutions,[70] still has not allowed recording of structured spectra for the molecules under study (β-TCDD, 1,3,7,8-Cl_4DD and OCDD).[58]

The most complete experimental data, reported in the literature, on the deactivation of the S_1 state for solutions of DD in isopentane [29, 56] and ethanol [71] are presented below.

ϕ_{fl}	τ_{fl}/ ns	k_{fl}/ s^{-1}	Ref.
0.003	3.5	0.9×10^6	56
0.000	< 1	–	71
–	–	1.6×10^7	29

For β-TCDD, an approximate estimate gave $\tau_{fl} \approx 10$ ns (vapour, 473 K) [58] and $k_{fl} \approx 4.0 \times 10^7$ s^{-1} (vapour and a solution in $CHCl_3$, 77 K).[29] The difference between the given ϕ_{fl} and τ_{fl} values determined for DD in the publications cited is due to the fact that the measurements were performed near the limit of the capacity of the equipment employed and to the influence of the solvent.

The k_{fl} values for isopentane solutions of DD have been determined by different methods.[29, 56] For DD (as well as for β-TCDD), the k_{fl} values for the $S_1(B_{2u}) \rightarrow S_0$ transition were estimated [29] using the calculated data on the ratio of the oscillator strengths of the $^1B_{2u} \leftarrow S_0$ and $^1B_{1u} \leftarrow S_0$ transitions, which are responsible for the long-wavelength band **A** in the absorption spectra, and experimental data on the integrated intensity of this band (see Figs 5, 6). The k_{fl} values found in this way are overestimated because the integrated extinction coefficient of band **A** can contain contributions of the transitions caused by the Herzberg–Teller vibronic coupling. In another method,[56] the k_{fl} value was estimated from the expression $k_{fl} = \phi_{fl} / \tau_{fl}$.

It is difficult to explain this great (by an order of magnitude) discrepancy of the k_{fl} values found for DD. The main reason may be as follows. One value [29] corresponds to the dipole-allowed $^1B_{2u} \rightarrow S_0$ transition. The other, smaller k_{fl} value [56] might refer to the emission from a *g*-type rather than *u*-type S_1 singlet state, for example, to the $^1A_g \rightarrow S_0$ transition, *i.e.* to a transition allowed only with account of the Herzberg–Teller intramolecular interactions. Some possible errors both in spectral measurements and in quantum-chemical calculations should also be taken into account.

An interesting dependence of the fluorescence and phosphorescence quantum yields on the structural factor for the series DD, dihydroanthracene and xanthene has been found.[56]

	Dihydroanthracene	Xanthene	DD
ϕ_{fl}	0.26	0.26	0.003
ϕ_{ph}	0.14	0.14	0.4

Despite the fact that the dihydroanthracene and xanthene molecules have the same luminescence quantum yields, the ϕ_{fl} value for DD is much smaller. Meanwhile, the ϕ_{ph} value for DD is almost 3 times as great as those for dihydroanthracene or xanthene.

According to calculations,[56] the S_1 state in the xanthene and DD molecules can be assigned to the π/π^* type of orbital; the change in the π-electron density on the oxygen atoms in this state is nearly the same for these two molecules. Therefore, the sharp (by two orders of magnitude) decrease in the ϕ_{fl} value for DD with respect to xanthene is believed to be due to the higher rate constant for the $S_1 \rightsquigarrow T_j$ intersystem crossing (k_{isc}) in the case of DD.

It is known that the k_{isc} values for the transfer of energy between states of different orbital natures, $\pi\pi^*$ and $n\pi^*$ (or $\sigma\pi^*$), are several orders of magnitude higher than those for states with the same orbital nature ($\pi\pi^*$ and $\pi\pi^*$).[72] For this reason, the higher k_{isc} value found for DD was interpreted [56] by assuming that only DD posesses a T_j state of the $n\pi^*$ type the energy of which is very close to the energy of S_1. This arrangement is believed to be due to the lowering of the energy levels of the $n\pi^*$ states in this molecule (containing two oxygen atoms) with respect to those in the xanthene molecule (with one oxygen atom). However, it follows from the calculations for the $n\pi^*$, $\pi\sigma^*$ and $\sigma\pi^*$ states that the energies of the corresponding triplet levels of the DD

molecule are more than 10 000 cm^{-1} higher than the energy of the S_1 state.[29,65] These states cannot ensure high k_{isc}. The difference between the ϕ_{fl} values in xanthene and DD might be due to the difference between the symmetries of the xanthene (C_{2v}) and DD (D_{2h}) molecules, in particular, to the fact that the S_1 state in the DD molecule might correspond to the *g* type: the first line in the spectrum of the $S_1 \leftarrow S_0$ transition shown in Fig. 7 has a relatively low intensity. In our opinion, the question of what is the reason for the low ϕ_{fl} value in DD remains open.

b. Phosphorescence

Phosphorescence is manifested as a relatively intense band in the spectrum shown in Fig. 8. Using specific experimental conditions, spectra with clear-cut vibrational structure of this band have been obtained for DD and PCDD (see Section V.2).

For a number of dioxins, the phosphorescence lifetimes τ_{ph} at 77 K have been measured.[2,43,56,64,65,73] For example, in the case of DD, $\tau_{ph} = 0.54$ s (77 K, a solution in a 1 : 5 : 5 mixture of ethanol, isopentane and ether)[2] and 0.7 s (77 K, a solution in isopentane).[56] For chloro-substituted derivatives, the phosphorescence lifetimes are shorter than for unsubstituted DD.[2]

In the case of PCDD, the τ_{ph} values found by different researchers can be substantially different. Thus for a number of dioxins (ranging from mono- to octa-substituted derivatives), τ_{ph} values varying from 0.29 to 0.075 s have been reported.[2] According to another publication,[73] the τ_{ph} values for another series of tetra- and penta-substituted dioxins in n-hexane vary over the 1.55 – 1.03 s range. The τ_{ph} values presented in the two publications[2,73] for the only compound common to both of them, 1,2,3,4-Cl_4DD, differ by more than an order of magnitude — 0.057 and 1.03 s. Both groups of researchers noted little differences in the τ_{ph} values within the series of dioxins they studied. Shorter τ_{ph} values were found[2] for those dioxins which contain several (3 or 4) Cl atoms in only one benzene fragment.

The great discrepancies between τ_{ph} found for PCDD in different studies are apparently due to some systematic error of measurements (rather than to the use of different solvents). For OCDD, β-TCDD and α,β-TCDD as solutions in n-hexane, the times τ_{ph} have been measured (see below) at 77 K.[43,64,65] These values were found to be in satisfactory agreement with τ_{ph} measured for solutions in a 1 : 5 : 5 mixture of ethanol, isopentane and ether.[2]

	OCDD	β-TCDD	α,β-TCDD
n-Hexane			
τ_{ph}/ s	0.30	0.20	0.30
Solvent mixture			
τ_{ph}/ s	0.25	–	0.25

The radiative $T \rightarrow S_0$ transitions are allowed due to intramolecular spin-orbit (SO) and vibronic-spin-orbit (VSO) couplings.[74,75] Correspondingly, the rate constant k_{rad} for the radiative deactivation of the triplet state can be represented as $k_{rad} = k_{SO} + k_{VSO}$; in the case of phosphorescence, $T = T_1$ and $k_{rad} = k_{ph}$. It has been proposed to use the data on the distribution of the intensity in fine-structure electronic-vibrational phosphorescence spectra for estimating the k_{VSO} to k_{SO} ratio.[76] These estimates obtained for the T_1 states of DD, β-TCDD and OCDD show[42] that the magnitudes of the phosphorescence rate constants k_{ph} for these molecules are stipulated by different mechanisms of intramolecular interactions. More precisely, this constant for DD is determined by only vibronic-spin-orbit coupling, while in β-TCDD and OCDD, they are determined by both spin-orbit and vibronic-spin-orbit couplings (see Section V.2).

Let us dwell now on the data on k_{ph}. It follows from the τ_{ph} and ϕ_{ph} values measured for the DD molecule[56] that $k_{ph} = 0.57\ s^{-1}$, $k_{SO} = 0$; hence, $k_{ph} = k_{VSO}$. For PCDD, no experimental data on k_{ph} are currently available, although the τ_{ph} values are known; they can be found from the relation

$$\tau_{ph} = \frac{1}{k_{ph} + k_{nr}^{T}},$$

where k_{ph} is the rate constant for the radiative and k_{nr}^{T} is the rate constant for the non-radiative deactivation of the T_1 state. For several dioxin molecules, the k_{SO}, k_{VSO} and k_{ph} values have been estimated theoretically.[43,64,65]

Quantum-chemical calculations were employed to estimate the k_{SO} values for DD, β-TCDD, α,β-TCDD and OCDD; it was found[43,64,65] that the number and the arrangement of Cl atoms in the molecule influences k_{SO} values for the $^3B_{1u}$ states. First, it was concluded that each heteroatom (O, α-Cl or β-Cl) in these molecules makes an additive contribution to the dipole moment of the $P_{0\text{-}0}$ transition (the square of which is related to k_{SO}). Second, a cancellation effect of the α-Cl and β-Cl atoms on the $P_{0\text{-}0}$ value was found. As a result, it was found that k_{SO}(β-TCDD) / k_{SO}(OCDD) = 3.6, *i.e.* the decrease in the number of Cl atoms in the molecules of β-TCDD with respect to that in OCDD (by a factor of two) induces a substantial increase rather than a decrease in the k_{SO} component of the k_{rad} rate constant. It was concluded[43,65] that the cancellation effect of several heteroatoms (chemically identical but differing in the position in the molecule) on the spin-orbit coupling, found in the study of dioxins, could be useful in elucidating the reasons for the known abnormal influence[77,78] of an internal heavy atom on the k_{ph} and τ_{ph} values in some organic molecules.

The use of calculated k_{SO} values and experimental data on the k_{SO} / k_{VSO} ratio gave the following estimates for the rate constants k_{ph} for β-TCDD and OCDD: 7 and 5 s^{-1}. Modelling of the k_{nr}^{T} values made it possible to determine theoretically[64] the ratio of τ_{ph} for these molecules [τ_{ph}(OCDD) / τ_{ph}(β-TCDD) = 1.6 ± 0.2], which is consistent with the experimental value 1.5 (the experimental data on τ_{ph} were mentioned above). The theoretical absolute magnitudes of τ_{ph} for these molecules also proved to be close to experimental values. For instance, for OCDD, the calculated value was τ_{ph} = 0.10 – 0.20 s.

2. Fine-structure phosphorescence spectra

In this Section, we consider the results of investigations of fine-structure phosphorescence spectra of dioxins concerning the energies and types of symmetry of lower triplet electronic states, the frequencies and types of symmetry of vibrations (in particular, low-frequency vibrations), and the contributions of intramolecular spin-orbit and vibronic-spin-orbit couplings to the phosphorescence rate constant. The results of theoretical calculations for the change in the electron density and the estimates of the change in the molecular geometry in the lower excited triplet ππ* state with respect to the ground electronic state are presented.

a. Spectra at 77 K

Below we consider experimental data on the influence of solvents (non-branched alkanes) on the pattern of the low-temperature phosphorescence spectra of dioxins.

The fine structure of broad-band phosphorescence spectra (see, for example, Fig. 8) can be recorded under specific conditions, which include conducting the experiment at low temperatures, selection of the appropriate solvent and, in some cases, selection of a particular wavelength of the exciting light.[70,79] These experimental conditions should ensure low electron – phonon interactions and slight inhomogeneous or homogeneous spectral broadening.[70,80] A well-known method for recording the structured luminescence spectra of complex organic compounds is the Shpol'skii method,[79] based on the use of n-alkanes (n-hexane, n-heptane, n-octane, *etc.*), which form a polycrystalline material at low temperatures, as solvents. These solvents ensure slight inhomogeneous broadening of the spectrum. Upon deep cooling of solutions of luminescent molecules in these solvents down to the boiling point of liquid nitrogen (77 K) or liquid helium (4.2 K), the electron – phonon interaction and homogeneous broadening of the spectrum decrease.[80] As a con-

sequence, the electronic-vibrational (vibronic) emission spectra consist of a large number of quasi-lines (lines). These spectra are referred to as quasi-line or fine-structure spectra.

The vibrational structure of the phosphorescence spectra of DD and PCDD was revealed at 77 K for solutions in a 1 : 5 : 5 mixture of ethanol, isopentane and ether [2] and in normal hydrocarbons.[81, 82] When the Shpol'skii method is used to make the structure of the spectrum as clear as possible at a specified temperature, it is important to select an appropriate solvent. The Bolotnikova rule [83] concerning the commensurability of the linear dimensions of the molecules of the solvent and of the compound under study serves as a criterion for choosing the solvent. Since dioxins are highly toxic, the problem of selecting the solvent has been studied in detail only for DD.[81] It was established that the most clear spectrum is observed in n-hexane and n-heptane matrices (Fig. 9). The spectral patterns in these solvents are more structured than in a 1 : 5 : 5 mixture of ethanol, isopentane and ether.

The structured phosphorescence spectra of solid solutions exhibit so-called components of the Shpol'skii multiplet, which are due to luminescence of different centres. Each of the luminescence centres is matched by lines for transition to vibrational sublevels of the ground electronic state (this is the vibronic structure of the spectrum) and by a line corresponding to a purely electronic transition (if it is dipole-allowed) with the frequency $\nu_{0\text{-}0}$. As a consequence, the spectrum often has a very intricate structure. At 77 K, the lines are normally markedly broadened due to the phonon wing and they are often called quasi-lines.[62, 70]

Table 6 lists the quasi-line maxima (1 – 9) in the spectra of DD and PCDD;[82] only for 1,2,3,4,6-Cl_5DD was it impossible to obtain a quasi-line spectrum in solid solutions in hydrocarbons. The spectrum of this compound was a broad structureless band with a maximum at 480 nm. The same spectral pattern with a maximum at 485 nm was obtained for solutions of 1,2,3,4-Cl_4DD in a 1 : 5 : 5 mixture of ethanol, isopentane and ether and in n-hexane at 77 K.[2, 73]

Now we consider briefly the possible reason for the absence of structure and the bathochromic shift of the phosphorescence band in the spectra of solutions of 1,2,3,4-Cl_4DD [2, 73] and 1,2,3,4,6-Cl_5DD.[82] A specific feature of these molecules is that one benzene ring in them is fully chlorinated, while the other contains either no chlorine atoms or only one atom. Molecules with so asymmetric an arrangement of chlorine atoms are polar.

It has been shown that polar molecules of oxygen-containing compounds dimerise in solutions in saturated hydrocarbons.[84] Thus the broad structureless bands in the phosphorescence spectra of 1,2,3,4-Cl_4DD and 1,2,3,4,6-Cl_5DD may belong to their dimers. However, to elucidate more definitely the reason for the structure-

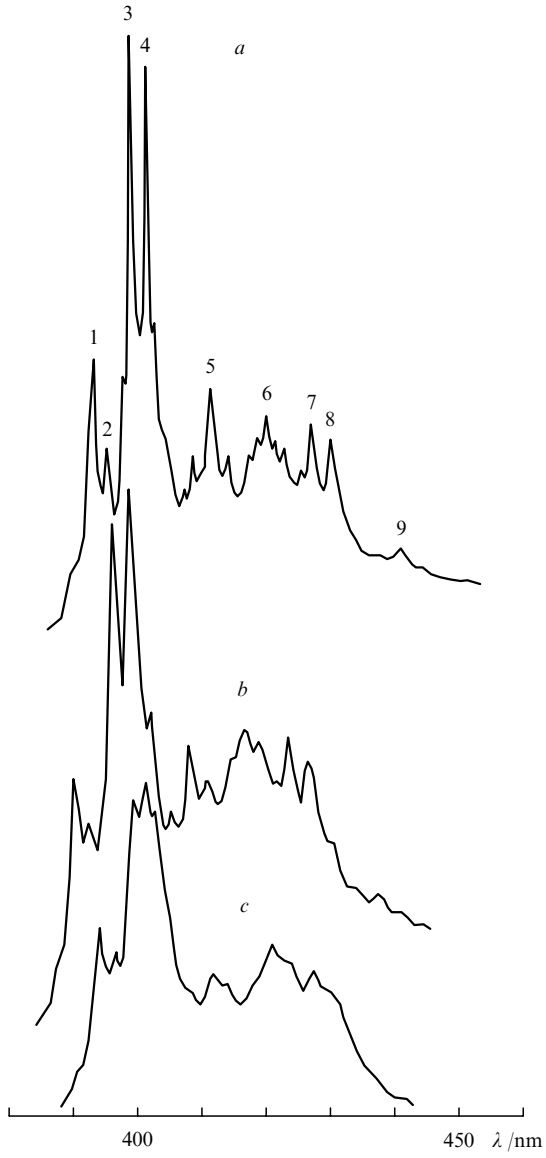


Figure 9. Phosphorescence spectrum of solutions of DD in n-hexane (*a*), n-heptane (*b*) and n-octane (*c*) at 77 K.[81] The λ values in the maxima of the numbered lines are given in Table 6.

Table 6. Positions of the quasi-line maxima in the phosphorescence spectra of solutions of dioxins in n-hexane at 77 K.[82]

Compound	λ/ nm								
	1	2	3	4	5	6	7	8	9
DD	394	396	**400**	**402**	412	420	427	430	441
2-ClDD	396	399	**402**	408	410	414	**424**	430	
2,3-Cl_2DD	402	**406**	407	412	**416**	**429**			
2,3,8-Cl_3DD	**403**	**407**	**408**	410	415	418	**432**		
2,3,7,9-Cl_4DD	**406**	**410**	412	417	420	428	434	438	
2,3,8,9-Cl_4DD	**406**	407	**410**	**417**	428	434	439		
β-TCDD	**410**	412	417	421	433	**438**	441	447	
α,β-TCDD	**409**	**411**	415	417	419	426	433	437	440
1,2,3,7,8-Cl_5DD	410	**413**	415	**421**	436	**442**	451		
1,2,3,4,6-Cl_5DD	480								
1,2,3,4,7,8-Cl_6DD	**408**	415	**420**	426					
1,2,3,6,7,8-Cl_6DD	**414**	**417**	**424**	440	443	446			
OCDD	419	423	**430**	436	443	449	**454**	462	

Note. The numerals 1 to 9 mark the numbers of lines in the spectra. The wavelengths corresponding to the most intense quasi-lines in the phosphorescence spectra are typed in bold.

less spectral pattern and the bathochromic shift of the phosphorescence band in the spectra of these compounds with respect to the spectra of other PCDD, additional investigations are needed.

Data on the positions of the quasi-line maxima in the spectra and on the distribution of the relative intensities of quasi-lines led to the conclusion [82, 85] that these spectra are highly individual and could be used for identification of various dioxins, in particular, isomers (see Section VI).

b. Spectra at 4.2 K

Study of the phosphorescence spectra of a number of dioxins at 4.2 K (see compounds in Table 6) showed [82] that, as the temperature decreases from 77 to 4.2 K, the half-width of the quasi-lines decreases by an order of magnitude (to 0.2–0.5 nm), while the peak intensity of lines increases. In addition, whereas the spectra recorded at the boiling point of liquid nitrogen consist, on the average, of 10–15 quasi-lines, the spectra at 4.7 K contain several dozens of quasi-lines.

At low temperatures (for example, 4.2 K), the vibronic structure of the emission spectra is due to the transitions from the zero vibrational sublevel of the electronically excited state to various vibrational sublevels of the ground electronic state S_0. This spectrum contains vibration frequencies which are detected in the vibrational spectra (IR and Raman). As an example, Figure 10 shows a fine-structure phosphorescence spectrum of a solution of DD, while Table 7 presents the assignment of the structure of this spectrum,[41] namely, determination of the components of the Shpol'skii multiplet, the frequencies of purely electronic transitions $\nu_{0\text{-}0}$, the frequencies of the fundamental vibrations and the sum vibration frequencies. A similar analysis of the spectral structure has been carried out for solutions of β-TCDD, α,β-TCDD and OCDD.[39, 42, 43]

The $T_1 \rightarrow S_0$ transition, which is spin forbidden, becomes allowed as a result of spin-orbit and vibronic-spin-orbit couplings.[74, 75] As a consequence, the fine-structure electronic spectra do not exhibit all vibrations but only totally symmetric vibrations and some types of non-totally symmetric ones. By taking account of the characteristic matrix elements [72] for the spin-orbit coupling and of the dipole moments of the $^1\sigma\pi^* \rightarrow S_0$ and $^1\pi\pi^* \rightarrow S_0$ transitions, which influence the line intensity, it can be concluded [30] that the out-of-plane vibrations may be responsible for intense lines in the ππ* phosphorescence spectra. Vibronic lines of this type are actually observed in the phosphorescence spectra of dioxins (see Figs 10, 11 and Table 7).

Determination of the symmetry of the T_1 state in dioxins is difficult. According to quantum-chemical calculations,[29, 65] the two ππ* triplet states lowest in energy (more precisely, $\pi l\pi^*$) correspond to electronic functions of *g* and *u* types, the *T* state of the *u* type being analogous in orbital structure to the fourth ππ* singlet state $S_4(B_{1u})$, the band of which is 'hidden' in the long-wavelength absorption band (see Figs 5, 6). The difference between the energies of the two *T* states is small ($\sim 1000\ cm^{-1}$); hence, variation of the positions of chlorine atoms in PCDD molecules can change the mutual arrangement of these triplet states. However, the accuracy of calculations does not suffice for deciding which of the states with the calculated types of symmetry B_{3g} and B_{1u} is the lowest (T_1). Moreover, the ππ* phosphorescence spectra of dioxins the molecules of which have an inversion centre can exhibit intense lines corresponding to out-of-plane vibrations for both symmetry forbidden (when T_1 belongs to the *g* type of symmetry) and symmetry allowed (when T_1 belongs to the *u* type of symmetry) transitions.

The question of the type of symmetry of the T_1 state can be answered by determining the type of symmetry of non-totally symmetric vibrations the frequencies of which ν(phos) are observed in the phosphorescence spectra. For the $T_1 \rightarrow S_0$ transitions from the states corresponding to *g* or *u* symmetry, non-totally symmetric (out-of-plane) vibrations of only a particular type of symmetry, either *u* or *g*, respectively, can manifest themselves, in conformity with the selection rules.[75] This regularity was used [39, 41–43] to determine the type of symmetry of the T_1 state of dioxins. These states in DD, β-TCDD and OCDD were assigned to different (B_{3g} and B_{1u}) types of symmetry (Fig. 12). The experimental values of the energies ($\nu_{0\text{-}0}$) of the T_1 state and the corresponding k_{SO}/k_{VSO} ratios for the components of the phosphorescence rate constants have also been determined for these compounds.[42]

	DD	β-TCDD	OCDD
$\nu_{0\text{-}0}$ /cm^{-1}	25595	24410	23836
$k_{SO} : k_{VSO}$	0 : 1	1 : 0.7	1 : 3.3

The $\nu_{0\text{-}0}$ frequencies of purely electronic transitions, $T_1 \rightarrow S_0$, either allowed or forbidden from the orbital symmetry standpoint,

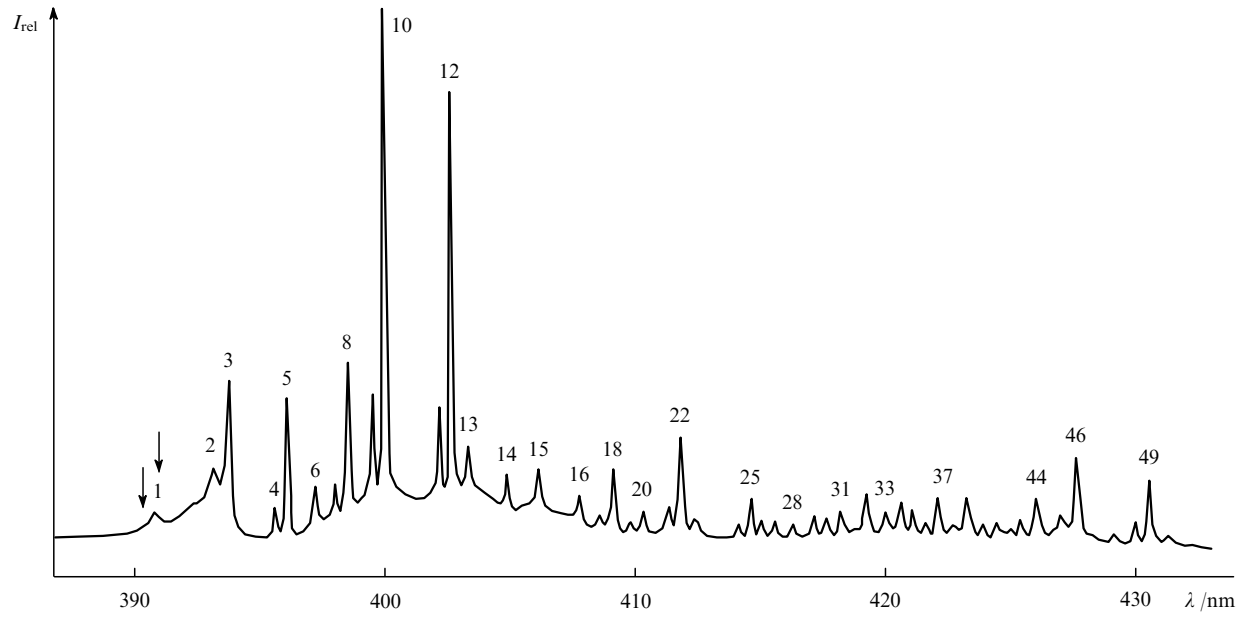


Figure 10. Phosphorescence spectrum of DD in n-hexane at 4.2 K.[41] The interpretation of the spectrum is given in Table 7. The arrows mark the positions of the Shpol'skii multiplet components corresponding to a purely electronic transition.

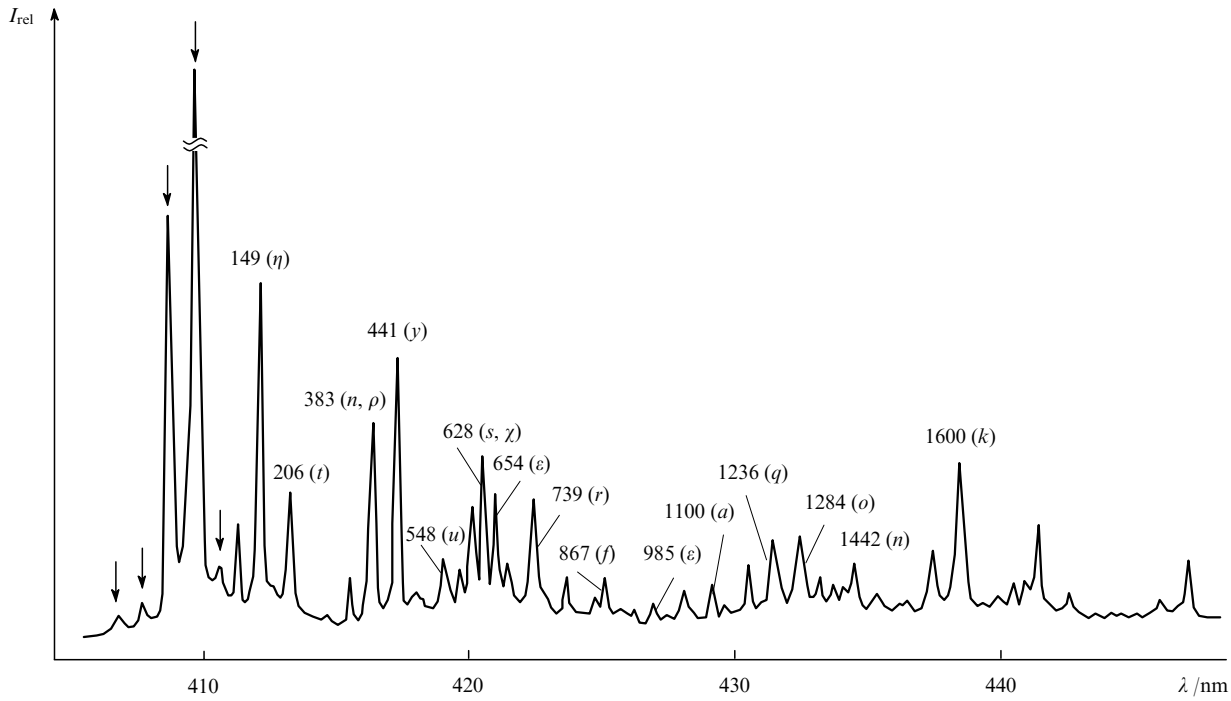


Figure 11. Phosphorescence spectra of β-TCDD in n-hexane at 4.2 K.[39] The arrows mark the positions of the Shpol'skii multiplet components corresponding to a purely electronic transition. In the line maxima of the most intense multiplet components, the frequencies (cm^{-1}) of only fundamental modes are given. The assignment of vibrations is given in parentheses (see Table 1).

Table 7. Positions of the line maxima (ν_N/ cm^{-1}) and interpretation of the phosphorescence spectra of DD in n-hexane (see Fig. 10).

Line number N	ν_N/ cm^{-1}	Components of the Shpol'skii multiplet	$\Delta\nu$ [a]	Interpretation [b]	Line number N	ν_N/ cm^{-1}	Components of the Shpol'skii multiplet	$\Delta\nu$ [a]	Interpretation [b]
	25628	I	0	0-0	25	24134	II	1461	$\nu_5 + \nu_{10}$ (722)
1	25595	II	0	0-0	26	24116	II	1479	?
2	25439	I	189	ν_1 (*h*)	27	24081	II	1514	?
3	25407	II	188	ν_1 (*h*)	28	24035	II	1560	?
4	25296	I	332	ν_2 (*y*)	29	23992	II	1603	$\nu_4 + \nu_{11}$ (1027)
5	25266	II	329	ν_2 (*y*)	30	23964	II	1631	$\nu_3 + \nu_{12}$ (1146)
6	25188	III		0-0 ?	31	23931	II	1664	?
7	25141	I	487	ν_3 (χ)	32	23873	II	1722	$\nu_4 + \nu_{12}$ (1146)
8	25110	II	485	ν_3 (χ)	33	23830	II	1765	$\nu_5 + \nu_{11}$ (1026)
9	25052	I	576	ν_4 (ω)	34	23792	II	1803	$\nu_4 + \nu_{13}$ (1227)
10	25019	II	576	ν_4 (ω)	35	23766	II	1829	?
11	24887	I	741	ν_5 (*g*)	36	23738	I	1890	$\nu_5 + \nu_{12}$ (1149)
12	24856	II	739	ν_5 (*g*)			II	1857	$\nu_4 + \nu_9 + \nu_{10}$ (715)
13	24814	II	781	ν_6 (υ)	37	23710	II	1885	$\nu_5 + \nu_{12}$ (1146)
14	24719	II	876	ν_7 (*i*)	38	23672	I	1956	$\nu_5 + \nu_{13}$ (1215)
15	24639	II	956	ν_8 (*j*)	39	23646	II	1949	$\nu_5 + \nu_{13}$ (1210)
16	24535	II	1060	$\nu_3 + \nu_9$ (575)					$\nu_2 + \nu_{14}$ (1620)
17	24484	I	1144	$\nu_4 + \nu_9$ (568)	40	23610	II	1985	?
18	24453	II	1142	$\nu_4 + \nu_9$ (566)	41	23571	II	2024	$\nu_5 + \nu_9 + \nu_{10}$ (719)
19	24418	II	1177	?	42	23544	II	2051	?
20	24383	II	1212	$\nu_3 + \nu_{10}$ (727)	43	23520	I	2108	$\nu_3 + \nu_{14}$ (1621)
21	24325	I	1303	$\nu_4 + \nu_{10}$ (727)	44	23491	II	2104	$\nu_3 + \nu_{14}$ (1619)
				$\nu_5 + \nu_9$ (562)	45	23428	I	2200	$\nu_4 + \nu_{14}$ (1624)
22	24295	II	1300	$\nu_4 + \nu_{10}$ (724)	46	23396	II	2199	$\nu_4 + \nu_{14}$ (1623)
				$\nu_5 + \nu_9$ (561)	47	23312	II	2283	?
23	24264	II	1331	?	48	23269	I	2359	$\nu_5 + \nu_{14}$ (1618)
24	24164	I	1464	$\nu_5 + \nu_{10}$ (723)	49	23240	II	2355	$\nu_5 + \nu_{14}$ (1616)

[a] $\Delta\nu = \nu_{0\text{-}0} - \nu_N$, where $\nu_{0\text{-}0}$ is the frequency of the purely electronic transition. [b] The ordinal number L of the fundamental mode found in the phosphorescence spectrum is given. The frequencies ν_L, separated from the sum frequencies, with the numbers $L = 9-14$ correspond to totally symmetric fundamental vibrations (their frequencies are given in parentheses); the frequencies ν_L with the numbers $L = 1-8$ were assigned to out-of-plane vibrations of the B_{3u} and A_u types of symmetry (their letter designations are given in parenheses).

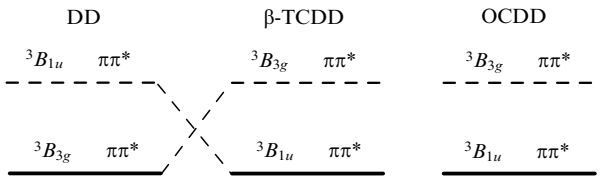


Figure 12. Symmetry of the T_1 and T_2 electronic states.[42]

decrease somewhat in the sequence DD, β-TCDD and OCDD [39, 41–43] (the values presented above are the $v_{0\text{-}0}$ frequencies of one or several components of the Shpol'skii multiplet, which accounts for the most intense vibronic lines in the spectrum).

The out-of-plane vibrations of dioxins are characterised by low frequencies which are unknown from IR or Raman spectra for the vast majority of dioxins. Therefore, in the absence of experimental data, the symmetry types of the vibrations the frequencies of which v(phos) can be seen in the phosphorescence spectra can be determined by comparing the calculated vibration frequencies with v(phos). Generally, this comparison provides a satisfactory result (see the phosphorescence spectrum of β-TCDD shown in Fig. 11 and the data on the frequencies of the fundamental modes in β-TCDD listed in Tables 2–5).

The most complicated problem is to interpret the phosphorescence spectra corresponding to a forbidden purely electronic transition because in this spectrum, it is difficult to find lines due to the components of the Shpol'skii multiplet and $v_{0\text{-}0}$ (see, for example, Fig. 10 and Table 7, data for DD). The positions of lines corresponding to the $v_{0\text{-}0}$ frequencies are determined from the v(phos) values for non-totally symmetric vibrations. Therefore, to interpret these spectra, reliable experimental (from IR or Raman spectra) or theoretical data on the low-frequency vibrations of the molecule are needed.

According to the results of quantum-chemical calculations,[43, 65] the $T_2(B_{1u})$ state of the DD molecule and the $T_1(B_{1u})$ state of the β-TCDD, α,β-TCDD and OCDD molecules are very close in orbital structure and are charge transfer states. For β-TCDD, the changes in the π-electron density on atoms and on valence bonds in the T_1 state with respect to those in the S_0 state (Fig. 13) have been calculated.[86] It was concluded that in this state, charge transfer takes place from all heteroatoms of the molecule to the carbon atoms; the electron density on the C–O bonds in the central fragment of the molecule increases, which implies that the bonds are shortened.

The data on the $v_{0\text{-}0}$ frequencies corresponding to the singlet S_1 state [23] and the triplet T_1 state (see Fig. 12) of DD and β-TCDD molecules in solutions can be used to estimate the difference between the energies of these states — 7430 and 6940 cm^{-1}. These values are typical of aromatic molecules with an electron-donating group;[69] this is consistent with the theoretical data on the pattern of electron density redistribution in the S_1 and T_1 states.

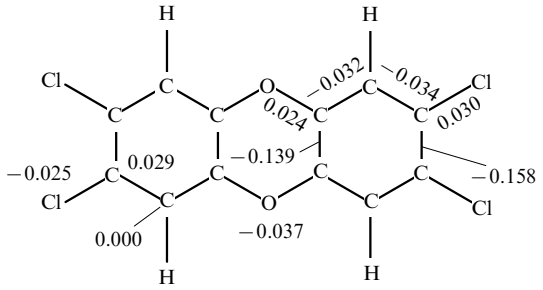


Figure 13. Changes in the electron density on the bonds and atoms of the β-TCDD molecule in the lower triplet excited state $^3B_{1u}$ (ππ*).[86] The values for only one of the equivalent atoms are presented.

The distribution of the intensity of vibronic lines in the fine-structure phosphorescence spectra depends on the intramolecular interactions.[62, 63, 87] The relative intensities of the vibronic lines with maxima at $v_{0\text{-}0} - v_N$ corresponding to the fundamental modes with the frequencies v_N were measured in the phosphorescence spectra of DD, β-TCDD, α,β-TCDD and OCDD.[39, 41–43]

The intensity distribution of the lines corresponding to totally symmetric vibrations is determined by the Franck–Condon interaction, which results in a changed equilibrium geometry of the molecule in the electronically excited state. The symmetry of the nuclear configuration typical of the S_0 state is retained. The change in the geometry induces a shift of the minimum of the electron potential (Δ_{el}) along the normal vibration coordinates Q.[62]

The Δ_{el} values were determined experimentally for the $T_1(^3B_{3g})$ electronic state of DD [28] and for the $T_1(^3B_{1u})$ electronic state of β-TCDD.[86] In the case of β-TCDD, the highest Δ_{el} value corresponds to the normal coordinate with the index η, which describes bending of the C–Cl bond in the plane of the molecule (see the letter designations of vibrations in Table 1). In each of these molecules, the highest Δ_{el} value for vibrations involving the benzene fragment corresponds to the normal coordinate Q_k, which is typical of electronic states of the B_{3g} or B_{1u} types (but not A_g or B_{2u}).[28, 30]

Using a simple theoretical model of the Franck–Condon interactions,[28] which reflects satisfactorily the experimental Δ_{el} values, the changes in the geometric parameters in the benzene fragments of DD and β-TCDD in the T_1 state have been calculated.[28, 86] It was found that the changes in the lengths of all bonds parallel to the z axis of the molecule [C(2)–C(3) and the three other] are about an order of magnitude greater than the changes in the other bond lengths in the benzene fragments. This is consistent with the results obtained by INDO/S calculations of electronic states (see Fig. 13). The changes in the bond lengths are nearly the same in each molecule and are equal to 0.021 and 0.027 Å for DD and β-TCDD, respectively. In β-TCDD, the C–Cl bonds are rotated in the molecular plane through 0.9°, according to an approximate estimate.[39]

The intensity of the region in the phosphorescence spectrum associated with the purely electronic transition and with totally symmetric vibrations is determined by the spin-orbit coupling, while the intensity of the other spectral region is governed by the vibronic-spin-orbit coupling.[75] Determination of the relative intensities of some lines in the spectrum provides [76] an experimental estimate of the contributions of spin-orbit and vibronic-spin-orbit couplings to the phosphorescence rate constant ($k_{ph} = k_{SO} + k_{VSO}$). The k_{SO}/k_{VSO} values were estimated for the T_1 state of DD, β-TCDD, α,β-TCDD and OCDD molecules.[39, 42, 43] The quantitative results obtained [39, 41–43] indicate that an increase in the number of Cl atoms in the molecule (β-TCDD and OCDD) sharply increases the contribution of the vibronic-spin-orbit coupling (with respect to the spin-orbit coupling) to the constant k_{ph}.

The lines corresponding to non-totally symmetric modes do not form progressions if they have originated due to the Herzberg–Teller interactions, *i.e.* if no change in the nuclear configuration of the molecule related to the change of its symmetry typical of the S_0 state is involved. However, apparently, it would be possible to establish correlations between the relative intensities of the vibronic lines caused by Herzberg–Teller interactions and the probable destruction processes of dioxins in photochemial reactions in the electronic state T_1. For instance, some correlations have been found between the intensity of vibronic lines related to non-totally symmetric vibrations of a particular form and the structural changes in the molecules of carbonyl-containing compounds upon photochemical reactions in the triplet ($n\pi^*$) and ($\pi\pi^*$) electronically excited states.[88]

VI. Spectroscopic analytical investigations

It has been mentioned in the Introduction that dioxins are formed as trace side products in some industrial processes including chemical (production of chlorinated phenols, herbicides and so on) and pulp-and-paper (paper bleaching) processes and during the operation of garbage-incineration plants. This is accompanied by dioxin pollution of the environment. Polychlorinated dibenzo-*p*-dioxins are highly stable compounds. They do not decompose at high temperatures (up to 750 °C); the half-life of PCDD in soil is about 10 years.[89] Due to their stability, the dioxin toxicants are accumulated in soil, water, plants and animals, which creates hazard for humans and other living organisms, because dioxins are many orders of magnitude more toxic than commonly known poisons (such as potassium cyanide or curare). Realisation of the dioxin menace stimulated the governments of many countries to adopt special programmes on the protection of the environment from these toxic compounds.

One aspect of the environmental protection is the development of highly sensitive methods for determination and quantitative analysis of traces of PCDD. Since dioxins are very hazardous compounds, methods for their analysis should be highly sensitive, at the picogram level. Yet another, equally significant requirement to the methods of dioxin analysis is high selectivity. This requirement originates due to the fact that dioxins having different structures differ markedly in toxic properties.[4, 90, 91]

Figure 14 presents the results of an experiment with guinea-pigs. It demonstrates how sharply (by approximately four orders of magnitude) the toxicity of PCDD containing from seven to four chlorine atoms increases as the α-Cl atoms are successively replaced by hydrogen atoms. The effect of PCDD on organisms is appreciably variable; however, generally, the regularity presented in Fig. 14 holds. Thus β-TCDD is considered to be the most toxic.

At present, toxicity equivalent factors (TEF)[91] common to humans and mammals have been established (for β-TCDD, TEF = 1). Apart from β-TCDD, six more PCDD containing four chlorine atoms in the β-positions are considered to be toxic. For example, for 1,2,3,7,8-Cl_5DD and the three isomers of hexachloro-substituted dibenzo-*p*-dioxins, TEF = 1 and 0.1, respectively; for the octasubstituted dibenzo-*p*-dioxin, TEF = 0.0001. Therefore, in monitoring the dioxin contamination, the problem of identification of the most hazardous PCDD is a crucial point. Identification is also important in connection with the need to determine precisely the reason (*i.e.* who is to blame) for the contamination and to control the process of dioxin destruction. From the scientific viewpoint, this is important for determining the mechanisms and the products of destruction of dioxins during incineration, photolysis and chemical or biological deactivation.

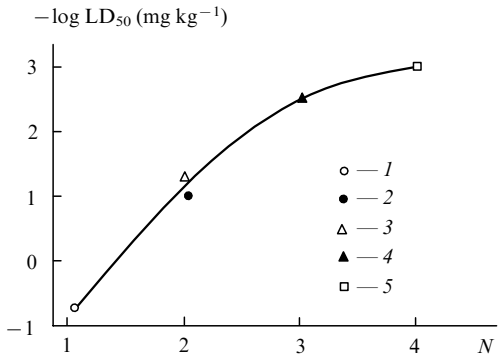


Figure 14. Toxicity of dioxins (the lethal dose LD_{50} for guinea-pigs) *vs.* the number (*N*) of hydrogen atoms occupying α-positions in the 1,2,3,4,6,7,8-Cl_7DD (*1*), 1,2,3,6,7,8-Cl_6DD and 1,2,3,7,8,9-Cl_6DD (*2*), 1,2,3,4,7,8-Cl_6DD (*3*), 1,2,3,7,8-Cl_5DD (*4*) and β-TCDD (*5*) molecules.[24]

The best developed and most widely used methods for analysis of dioxins not related to optical spectroscopy include various modifications of the chromatographic method,[92–95] chromato-mass spectrometry,[96–98] a method combining chromatographic separation of isomers with their NMR detection,[99] *etc.* Description of all the methods used currently is beyond the scope of this review. We shall restrict themselves to a brief description of the optical methods of analysis employed for this purpose.

Among optical methods, Fourier IR spectroscopy (FTIR) is used most extensively to analyse dioxins. Usually, this technique is combined with chromatographic methods.[98] Thus even in the first publications [32, 34] dealing with analysis of dioxins by gas chromatography and FTIR (GC-FTIR method), using reflectance and absorption spectra, the researchers were able to identify all the 22 isomers of tetrachloro-substituted dioxin. This method permits detection of dioxins present in concentrations of several hundreds of nanograms.

A higher sensitivity of the method can be attained by using matrix isolation of the analysed compounds (GC-MI-FTIR).[100] In this case, the isomers separated by chromatography were present in an argon matrix at 12 K; this decreases the line half-width and, correspondingly, increases the peak intensity of lines. The IR spectra of all the 22 isomers of tetrachloro-substituted dioxin were recorded by this method,[33, 35, 36] including the spectra of β-TCDD and its completely isotope-substituted analogue ([^{13}C]β-TCDD), in which all the ^{12}C atoms have been replaced by ^{13}C. This technique is suitable for the analysis of samples with contents of tetrachloro-substituted DD of the order of hundreds of picograms.[36, 100, 101] For example, the use of [^{13}C]β-TCDD as the internal standard permitted determination of β-TCDD in a concentration of 15–45 pg per g in an extract from a fish tissue.[37]

To identify dioxins on the basis of their IR spectra, several characteristic bands in the range of 1600–800 cm^{-1} are used.[24, 33, 35] Figure 15 presents the IR spectrum of the extract from a fish tissue containing β-TCDD and an internal standard admixed. Generally, the positions of bands in the spectrum recorded by the GC-MI-FTIR method coincide with the positions of the corresponding bands in the spectrum of β-TCDD in a KBr pellet (see Fig. 2).

Figure 16 shows an example of identification, based on IR bands, of two tetrachloro-substituted DD isomers which are poorly resolved by gas chromatography [102, 103] but are separated by gas liquid chromatography. In the frequency range of 1600–800 cm^{-1}, the positions of the maxima of bands in the spectra of these isomers differ only slightly; however, the isomers can be identified based on the different relative intensities of bands. It has also been proposed [24, 35] to identify isomers using the

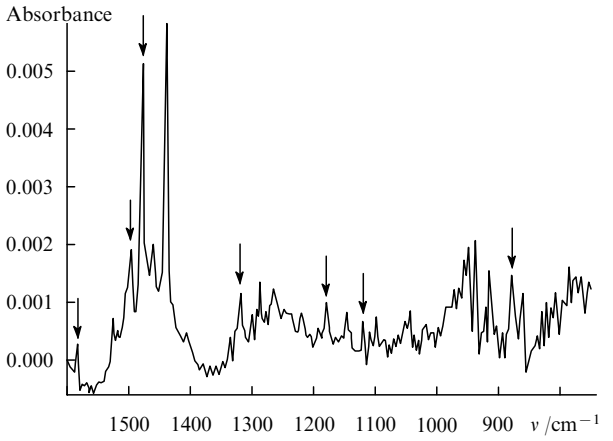


Figure 15. Absorption spectrum of the extract from a fish tissue containing β-TCDD and an admixture of [^{13}C]β-TCDD added as the internal standard. The spectrum was recorded by the GC-MI-FTIR technique; the analytical lines of the β-TCDD toxin [37] are marked by arrows.

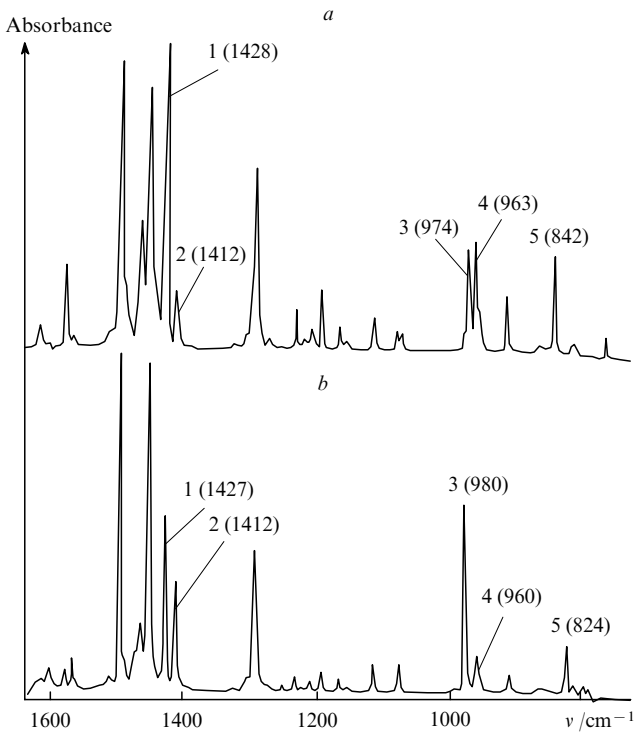


Figure 16. Absorption spectrum recorded by the GC-MI-FTIR method for the isomers 1,2,4,8-Cl_4DD (*a*) and 1,2,4,7-Cl_4DD (*b*).[35] The numerals 1–5 mark the analytical lines the relative intensities of which at 1420 cm^{-1} (lines 1, 2) and at 980–820 cm^{-1} (lines 3–5) can be used to indentify the isomers.

ν^{as}_{C-O} frequencies of the antisymmetric stretching vibrations of the C–O–C groups in the range of 1330–1280 cm^{-1}. However, in our opinion, this spectral region is less reliable for identification because the semiempirical triatomic model considered[35] determines the ν^{as}_{C-O} values too crudely; meanwhile, the difference between the experimental values of these frequencies for some pairs of isomers is very little (1–2 cm^{-1}).

The results of identification of PCDD isomers by four independent methods: chromatography, GC-MS, GC-FTIR and ^1H and ^{13}C NMR spectroscopy have been compared.[104] For several isomers, the results of identification did not coincide.

It has been proposed[22,47] to use the frequencies of normal modes of PCDD isomers found theoretically (by *ab initio* calculations) to identify the isomers based on their IR spectra.

Now we shall mention several other spectral methods for determination of dioxins. For example, theoretical estimates of the limits of detection of dioxins by Raman spectroscopy (~2 pg) and by giant Raman scattering (GRS, $\sim 2\times10^{-4}$ pg) allow the GRS method to be regarded as a promising analytical technique.[105] A simple photometric method based on the ability of PCDD to be protonated and to form coloured associates with transition metal anions has been proposed.[106] The lower limit of the β-TCDD concentration in a hexane extract determined by this method is 20 pg cm^{-3}.

The detection powers of the setups used in the studies of dioxins by UV absorption and fluorescence methods have been evaluated.[58,73] Fluorescence of dioxins shows itself as a broad band with a maximum in the region of 330–390 nm. For n-hexane solutions of PCDD containing 5 to 8 Cl atoms, the detection limit of the fluorescence analysis amounts to 0.5–5 ng cm^{-3} at room temperature for excitation with the wavelength λ_{excit} = 230–245 nm.[73] This spectrum region contains the maximum of band **B**, the most intense band in the UV absorption of dioxins (see Figs 5, 6). In laser-induced fluorescence analysis of dioxin vapours (β-TCDD, 1,2,3,7,8-Cl_5DD and OCDD) with λ_{excit} = 303 nm and at 170–270 °C, the detection limit was approximately four orders of magnitude lower; it was 0.09–0.13 pg cm^{-3} (see Ref. 58).

The detection power of the setup using the UV absorption method in the short-wavelength region (~224 nm) has been evaluated. The limit of detection of β-TCDD, 1,2,3,7,8-Cl_5DD and OCDD in vapours amounted to 8–90 pg cm^{-3} (see Ref. 58). It is noteworthy that the methods of detection mentioned above are not selective because the UV absorption and fluorescence bands of dioxins are very broad and, moreover, the maxima of these bands shift only slightly upon the change in the number of chlorine atoms in PCDD molecules (see Section IV).

The use of phosphorescence, more precisely, low-temperature quasi-line phosphorescence spectra of solid solutions, for identification of dioxins has also been proposed.[73,82,85] For example, it is known that the luminescence spectra recorded by this method (Shpol'skii method) have been used successfully to determine the content of polycyclic aromatic hydrocarbons as hazardous contaminants in foodstuffs and in non-edible oils.[107,108] The phosphorescence spectra of solid solutions of DD and many of PCDD in a 1 : 5 : 5 mixture of ethanol, isopentane and ether[73] at 77 K and in n-alkanes at 77 and 4.2 K[81,82,85] were shown to possess a quasi-line structure, the structures of spectra of different PCDD being substantially dissimilar (see Table 6). The differences are observed both in the positions of lines and in the intensity distribution. Thus, these spectra possess advantages over the structureless UV absorption and fluorescence spectra in the identification of compounds.

Figure 17 presents the phosphorescence spectrum (4.2 K) of a mixture of β-TCDD and α,β-TCDD isomers with concentrations

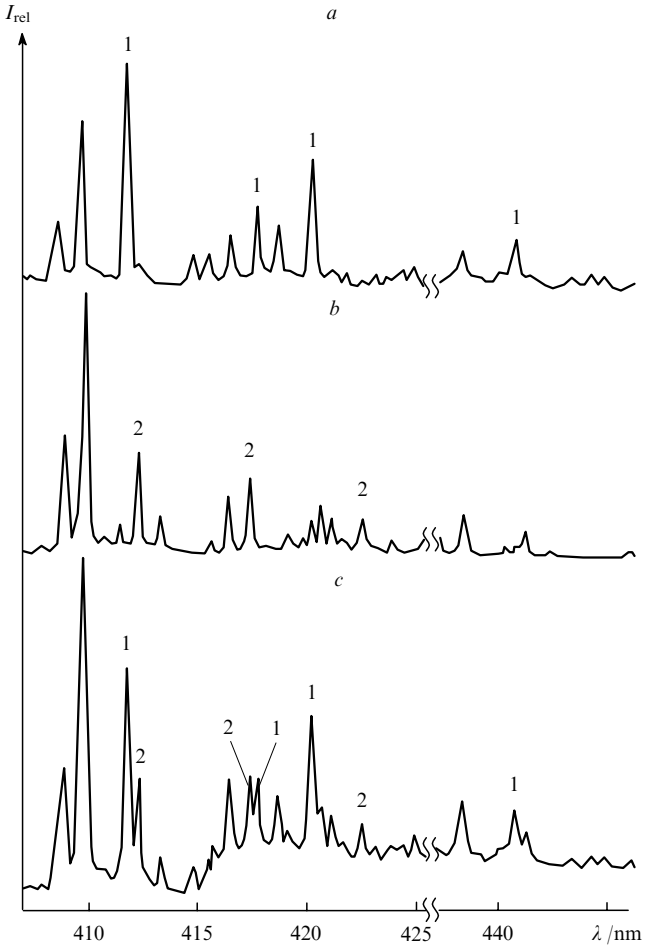


Figure 17. Phosphorescence spectra of α,β-TCDD (*a*), β-TCDD (*b*) and their mixtures (*c*) in n-hexane at 4.2 K.[82] In spectrum *c*, the analytical lines 1 and 2 corresponding to the two isomers (*a* and *b*) are marked.

of 4.5×10^{-5} and 3×10^{-5} mol litre^{-1}, respectively. The quasi-lines observed in the emission spectrum of a two-component solution can be assigned unambiguously to one of the mixture components, which is a clear illustration of the possibility of selective determination of isomers using these spectra. At 77 K, the phosphorescence spectra of PCDD isomers are less suitable for selective recording due to the greater ($\sim 2-4$ nm) half-width of bands. However, the simplicity of the equipment and the process of recording provides the possibility of developing a screening method for dioxin detection based on them.

The detection capacity of the spectral setups used for the detection of dioxins on the basis of quasi-line phosphorescence spectra has been evaluated.[73, 81, 82] At 77 K, for n-hexane solutions of dioxins containing 4 to 7 Cl atoms, the detection limit is $1-12$ ng cm^{-3} (see Ref. 73). The spectra of β-TCDD were found to be recorded reliably down to a concentration of 16 ng cm^{-3} (see Ref. 82). When analysing microvolumes of β-TCDD with recording of the most intense line in the spectrum ($\lambda = 410$ nm, see Table 6), determination of its amounts not lower than 100 pg is possible. It is expected that the limit of detection of tetrachloro-substituted DD could be markedly decreased by decreasing the temperature to 4.2 K, due to the increase in the peak intensity of vibronic lines.

The differences between the quasi-line phosphorescence spectra even for isomers with close structures and for PCDD with different numbers of Cl atoms gives hope that development of such a method would allow reliable identification of PCDD in complex mixtures.

VII. Conclusion

Since it is the molecular structure that accounts for the different photophysical properties of compounds, it is important to establish the geometrical structure of dioxins. X-Ray diffraction data point to a planar or nearly planar structure of DD and PCDD molecules in the crystals. No direct experimental data on the structures of these molecules in the gas phase or in solutions are available to date. Only indirect methods of determination do exist, relying on the data on the dipole moment of DD in solutions or on the results of theoretical calculations. Depending on the theoretical method of modelling employed, the equilibrium nuclear configuration of the molecule in the ground electronic state S_0 is found to be either planar or non-planar. In the case where the dioxin molecules are found to be non-planar, some researchers concluded that, in particular, DD has a 'butterfly' configuration. Data on the structures of dioxin molecules are contradictory. Some investigators who give credit to X-ray diffraction data believe that the dioxin molecules are planar; other researchers who rely on calculations consider that the molecules are non-planar. Note that the intramolecular vibration mode of the 'butterfly' type shows itself at a low frequency for all dioxins. Dioxin molecules might occur in different configurations depending on the experimental conditions (temperature, intermolecular interactions).

In some studies, attempts are made to relate different toxicities of PCDD to either planar or non-planar geometrical congfiguration. Spectroscopic methods of investigation are especially promising for the solution of the problem of the structure of dioxins (at least, four of them, DD, β-TCDD, 1,4,6,9-Cl_4DD and OCDD) which belong to the D_{2h} group of symmetry in the case of a planar configuration. Analysis of the IR and Raman spectra from the standpoint of selection rules could promote solution of the problem of the molecular configuration in the ground electronic state S_0. This type of analysis of the fine vibrational structure of the spectra recorded by electronic-vibrational spectroscopy methods (low-temperature UV absorption, hole burning, fluorescence, phosphorescence, excitation of luminescence) and by the resonance enhanced two-photon ionisation technique could facilitate solution of the problem (which has not yet been solved either) of the symmetry of the dioxin molecules in the S_1 and T_1 states. However, no comprehensive experimental and theoretical studies of dioxin vibrations that could answer the questions about the molecular configuration have been reported so far.

In view of the foregoing, one of the most important problems in the studies of dioxins is to investigate the intramolecular vibrations (both theoretically and experimentally). At present, almost no data on the Raman spectra are available. Despite the extensive use of IR spectroscopy for analytical purposes, data on low-frequency vibrations can scarcely be found in the literature. The results on the theoretical calculations that provide information on not only the frequencies but also the forms and types of symmetry of vibrations are also few. The data on the vibrations of dioxin molecules are also important for the interpretation of the fine vibrational structure of the electronic-vibrational spectra, in particular, phosphorescence spectra of solid solutions because the structure of these spectra is complicated by the presence of the Shpol'skii multiplet components. Interpretation of the vibrational structure of these spectra provides valuable information on the type of symmetry of the triplet electronic state, on the influence of chlorine atoms on the processes of photophysical deactivation of the electronically excited state and on the changes in the nuclear configuration of the molecule in this state.

Fourier Transform IR spectroscopy with matrix isolation of the molecule (combined with chromatography) is currently the main spectral method used to detect and identify dioxins. We believe that the Shpol'skii method would become yet another technique for the detection and identification of dioxins (at present, it is used for polycyclic aromatic hydrocarbons), provided that the light-gathering power of the equipment would be increased somewhat, for instance, by using FT spectrometers. At presence, the results of investigation of the fine-structure phosphorescence spectra of solutions of dioxins in non-branched alkanes at 77 and 4.2 K (using a standard spectrometer with diffraction gratings) confirmed the good prospects for using this technique for analytical purposes as a highly sensitive and selective method.

The knowledge of experimental photophysical characteristics of dioxins and their changes induced by particular factors (medium, temperature, *etc.*) is required not only for theoretical investigations of the mechanisms of deactivation of electronic states but also for the solution of some practical problems. Thus it is known that photochemical decomposition, which is supposed to proceed through a T_1 state, is the most effective process for the destruction of these toxicants. However, the available data on the photophysical studies of dioxins are obviously insufficient to provide optimisation of the methods for their photochemical deactivation. These data are also needed for searching for the ways of increasing the sensitivity of the spectral luminescence methods of analysis.

New data on the structure and properties of dioxins would help to disclose the mechanism of action of these ecotoxicants; they would enable further development and perfection of both analytical methods for the detection of dioxins and methods of environmental protection.

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