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FLUORESCENCE OF CHLOROTOLUENE VAPORS

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Fluorescence spectra, fluorescence quantum yields, and fluorescence lifetimes were measured for *o*-, *m*-, and *p*-chlorotoluene vapor. The radiative and non-radiative processes of excited chlorotoluene molecules are predominantly determined by the chlorine substitution and only slightly by the methyl substitution. The effect of the excess energy of excitation on the radiative and non-radiative transition rates is discussed in relation to the methyl and chlorine substitutions.

The measurements of the fluorescence decay rates of many methylated and fluorinated benzenes have revealed out that the fluorine substitution has rather drastic effects on the intersystem crossing than the methyl substitution.(1) More detailed studies on the photophysics of isolated fluorotoluene molecules have indicated several interesting differences among the three fluorotoluene isomers.(2-5) The dependence of the non-radiative transition rate on the number of quanta for the ν_1 vibrational mode in the *o*-fluorotoluene S_1 state is similar to that in the S_1 state of benzene. *p*-Fluorotoluene has faster radiative and slower non-radiative transition rates than other fluorotoluenes. *m*-Fluorotoluene has a rather larger triplet quantum yield than other fluorotoluenes.

We have previously reported the photophysics of isolated dichlorobenzenes.(6) *p*-Dichlorobenzene has also a rather long fluorescence lifetime and a high fluorescence quantum yield compared with other dichlorobenzenes when they are excited to low vibrational states of S_1. Slower non-radiative transitions and rather faster radiative transitions in *p*-disubstituted benzene relative to those in *m*- or *o*-disubstituted benzenes seem to be general trends in disubstituted benzenes.(7,8)

The purpose of the present paper is to report the photophysics of chlorotoluenes in order to examine the effects of the methyl group on the decay of excited chlorobenzenes. The experimental apparatus and techniques employed in this study are similar to those which have been reported elsewhere(6) except for the presence of cut-off filter placed between the cell and the photomultiplier which is a methanol solution (0.01 $\mathrm{mol \cdot dm^{-3}}$) of the sample and which eliminates the scattered excitation light. The use of the sample solution as the cut-off filter does not disturb the measurements of the vapor fluorescence and is effective to reduce the interference by the excitation light.

Fluorescence spectra of chlorotoluene vapors at a pressure of 0.6 Torr show distinct vibrational structures when they are excited at their 0-0 bands. The pressure and the fluorescence lifetimes (< 2 nsec) assure that excited molecules

Table I. Fluorescence quantum yields and lifetimes of chlorotoluenes.[a]

λ(nm)[b]	ΔE(cm^{-1})	Φ_f(x10^3)	τ_f(ns)	τ_r(ns)	τ_{nr}(ns)	Φ_f(x10^3)	τ_f(ns)
						Ethane:	760 torr
p-Chlorotoluene							
275.6	0[c]	31.0	1.6	52	1.7	25.4	1.2
272.7	357	18.8	1.1	59	1.1	18.9	1.2
271.3	544	16.3	1.0	61	1.0	18.2	1.2
269.8	762	16.8	1.4	83	1.4	20.5	1.0
267.7	1052	12.5	1.3	104	1.3	17.1	1.1
262.2	1052 + 762	9.1	0.9	99	0.9	11.8	1.2
m-Chlorotoluene							
273.3	0[d]	24.0	2.0	83	2.0	19.4	1.7
270.0	418	18.8	1.7	90	1.7	18.4	1.7
266.2	981	11.1	1.3	117	1.3	13.4	1.3
263.2	981 + 418	11.3	1.0	88	1.0	14.4	1.0
o-Chlorotoluene							
271.8	0[d]	23.0	1.5	65	1.5	20.0	1.5
268.0	530	17.9	1.1	61	1.1	20.4	1.5
264.7	1005	11.5	1.2	104	1.2	17.3	1.5
260.8	1005 + 530	6.9	0.9	130	0.9	10.6	1.2

a) Vapor pressures of chlorotoluenes are 0.6 torr throughout.

b) Excitation bandpass is 1 nm.

c) G. Viswanath, Indian J. Phys., 26 263 (1952).

d) H. N. Swamy, Indian J. Phys., 26 445 (1952).

	Φ_f	τ_f	τ_r	τ_{nr}
p-CB[a]	0.042	1.7	40	1.8
m-	0.016	1.3	83	1.3
o-	0.007	1.4	190	1.4
p-CT[b]	0.031	1.6	52	1.7
m-	0.024	2.0	83	2.0
o-	0.023	1.5	65	1.5

Table II. Fluorescence quantum yields and lifetimes(ns) of dichlorobenzenes and chlorotoluenes by 0-0 excitation.

a) Vapor pressures are 0.2, 0.4 and 0.2 torr for p-, m-, and o-dichlorobenzenes, respectively.

b) These values are from Table I.

are under collision free conditions. The vibrational structure is most pronounced with *p*-chlorotoluene. The vibrational structures of *o*-, and *m*-chlorotoluenes are more complicated than *p*-chlorotoluene. The vibrational structures disappear when molecules are excited at shorter wavelength than their 0-0 bands. This may be explained by an overlap of the complicated fluorescence vibrational structures from the higher vibrational levels in the fluorescent state and the excitation of closely lying levels due to insufficient resolution of the excitation or due to the migration of vibrational energy among various interacting vibrational modes. In the presence of ethane, the vibrational relaxation induced by molecular collisions diminishes the vibrational structures even in the 0-0 band excitation.

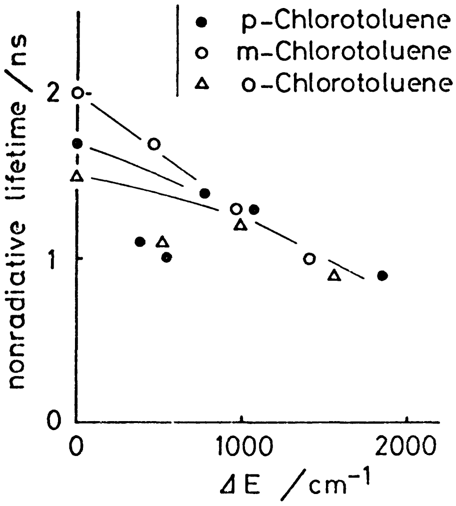

Fig. 1 Non-radiative lifetimes vs. excess vibrational energy. Vapor pressures of chlorotoluenes are 0.6 torr.

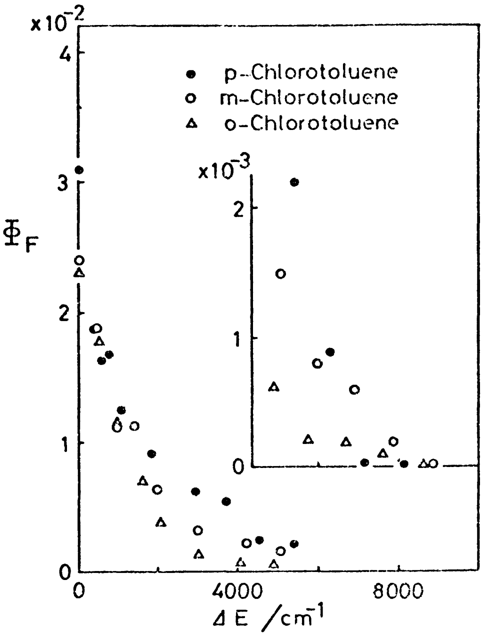

Fig. 2 Fluorescence quantum yields vs. excess vibrational energy. Above 4000 cm^{-1}, the scale of Φ_f is expanded in the insert.

Table I lists the observed fluorescence quantum yields (Φ_f) and the rates of radiative ($1/\tau_r$) and non-radiative ($1/\tau_{nr}$) transitions of chlorotoluene isomers in the absence and the presence of ethane. Values of Φ_f, τ_r and τ_{nr} for chlorotoluene isomers are similar to those of dichlorobenzenes.[6)] Table II shows those of chlorotoluenes and dichlorobenzenes observed with the 0-0 band excitation. The difference in values of chlorotoluene isomers is smaller than that in dichlorobenzenes. This fact indicates that the intramolecular processes in chlorotoluenes are rather insensitive to the position of substitution.

τ_r of chlorotoluene isomers have slowly increasing trends with the excess energy. The values of τ_r of the isomers at the excess vibrational energy about 1000 cm^{-1} are very similar. This is explained by the similarity of wavefunctions of chlorotoluene isomers in the ground and low lying electronically excited states. The wavefunctions would be essentially determined by the chlorine atom substituted into the benzene ring while the methyl substitution cannot cause significant modifications of wavefunctions.

The non-radiative transitions are supposed to be affected mainly by the chlorine substitution and also by the methyl substitution. As shown in Fig. 1, the values of τ_{nr}, however, are not strongly dependent on the position of methyl substitution though the three isomers have different values in the low excess energy regions. The non-radiative transitions in chlorotoluene isomers should be predominated by the intersystem crossing. The intersystem crossing rate in these excited levels is governed mostly by the electronic spin-orbit interaction, Franck-Condon factors, and level densities in the triplet manifold. Among chlorotoluene isomers, electronic spin-orbit interactions can not have much different values since the value is determined by the chlorine atom in the molecule. Therefore, the values of τ_{nr} should be determined by Franck-Condon factors and level densities. The results shown in Fig. 1 indicate that the Franck-Condon factors and the level densities for the intersystem crossing are almost the same for these isomers.

Fig. 2 shows the variation of fluorescence quantum yields of chlorotoluene isomers against the excess vibrational energy in S_1. At low excess energies three isomers have similar values though in higher excitation energies (excess vibrational energy 2000 $\sim$ 7000 cm^{-1}) they have different energy dependence. Chlorotoluenes undergo radiative or non-radiative process with similar transition rates at low excitation energies as discussed earlier. This leads to similar fluorescence quantum yields of chlorotoluene isomers at low excess vibrational energies. In higher excited levels vibronic interactions with S_2 or S_3 increase. This may cause differences in fluorescence quantum yields among chlorotoluene isomers.

In the presence of ethane, Φ_f and τ_f tend to approach limitting constant values, as shown in Table I. These results indicate that intermolecular collisions with ethane result in mostly vibrational relaxation in S_1 and very slight electronic quenching.

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