

# Laser-induced fluorescence of jet-cooled chlorotoluene molecules

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## Abstract

The laser-induced fluorescence spectra of jet-cooled *o*-, *m*- and *p*-chlorotoluene molecules in the S<sub>1</sub> state are reported. The fluorescence excitation spectra of these molecules exhibit a variety of vibrational modes in the S<sub>1</sub> state. The spectra of *m*- and *p*-chlorotoluene show low-frequency bands up to 200 cm<sup>-1</sup> above the S<sub>1</sub> origin, which are assigned to internal rotational modes of the methyl group. From 300 cm<sup>-1</sup> up to approximately 1500 cm<sup>-1</sup>, sharp vibrational bands appear; these are assigned by measuring the dispersed fluorescence spectra on excitation of each vibrational band. The vibrational energies of the C–Cl symmetric stretching mode for *o*-, *m*- and *p*-chlorotoluene molecules are 341 cm<sup>-1</sup>, 378 cm<sup>-1</sup> and 360 cm<sup>-1</sup> in the S<sub>1</sub> state respectively. Other prominent normal modes are also assigned.

**Keywords:** Laser-induced fluorescence; Jet-cooled chlorotoluene; Excitation spectra

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## 1. Introduction

Our interest in the photodissociation processes of chlorinated benzene derivatives was initiated by studies of the photolysis of monochlorobenzene vapour [1,2]. The photoexcitation of chlorotoluene vapour [3–6] to the first excited singlet state reveals that the excited molecules undergo intersystem crossing within a few nanoseconds to the triplet states, where decomposition and vibrational relaxation to the stable triplet state occur competitively. The absorption spectrum of chlorotoluene vapour becomes congested with hot vibrational and rotational bands.

Photofragment spectroscopy is a powerful method for investigating dissociation processes if the concentration of the photofragment is sufficiently high for detection. The dissociation mechanisms of chlorobenzene, chlorotoluenes and dichlorobenzenes excited at 193 nm have been investigated by this method [7–10]. These studies suggest that dissociation involves three channels: (1) a fast process taking place from the repulsive state; (2) a dominant slow dissociation process via a vibrationally excited triplet state; (3) the slowest decomposition occurring from the vibrationally hot ground state. The same method was applied to the dissociation of chlorobenzene at 248 nm [11]. The signal-to-noise ratio of the Cl fragment was quite low because the absorption cross-section at 248 nm is small.

In a preliminary paper, we have reported that laser-induced fluorescence techniques can be applied to jet-cooled *m*- and *p*-chlorotoluene molecules [12]. In this paper, we report the laser-induced fluorescence spectroscopy of *o*-, *m*- and *p*-chlorotoluene molecules. Prominent vibrational modes in the first excited singlet state (S<sub>1</sub>) have been assigned and the vibrational energy of the C–Cl symmetric stretching mode has been determined. The possibility that the mode selectivity enhances the non-radiative decay process is also discussed.

## 2. Experimental details

The apparatus for laser-induced fluorescence measurements has been described previously [13]. A pulsed supersonic free-jet nozzle was used to obtain the fluorescence excitation and emission spectra. Helium gas (backing pressure of 3 atm) was passed through the sample container (heated at 310 K to maintain sufficient vapour pressure), and the mixed gas was expanded into a vacuum chamber through an orifice of 0.8 mm in diameter. The pressure in the expansion chamber during a run at a repetition rate of 8 Hz was approximately 10<sup>-5</sup> Torr.

The fluorescence excitation spectra were obtained by monitoring the total fluorescence with a photomultiplier tube (Hamamatsu Photonics R-562). Signals from the photomultiplier tube were averaged by a boxcar integrator (Brookdeal 9415/9425) and recorded. The excitation source consisted

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of a frequency-doubled dye laser (Moletron DL-14P) pumped by a nitrogen laser (Moletron UV-24). The resolution of the excitation light was about  $1.0 \text{ cm}^{-1}$  (full width at half-maximum (FWHM)). Wavelength calibration was carried out using the fluorescence excitation spectrum of low-pressure iodine vapour.

The dispersed fluorescence spectra were obtained using a Nalumi 0.75 m monochromator with a 0.20 mm slit width. The spectral resolution was about  $10 \text{ cm}^{-1}$  (FWHM). Signals were detected by a photomultiplier (Hamamatsu Photonics R-928) and recorded by the same integrator system as used for the fluorescence excitation spectra.

Samples of *o*-, *m*- and *p*-chlorotoluene were purchased from Tokyo Kasei Ltd. and purified by distillation.

### 3. Results and discussion

#### 3.1. Vibrational band assignment

Fig. 1 shows the fluorescence excitation spectra of *o*-, *m*- and *p*-chlorotoluene in a supersonic free jet of 3 atm helium

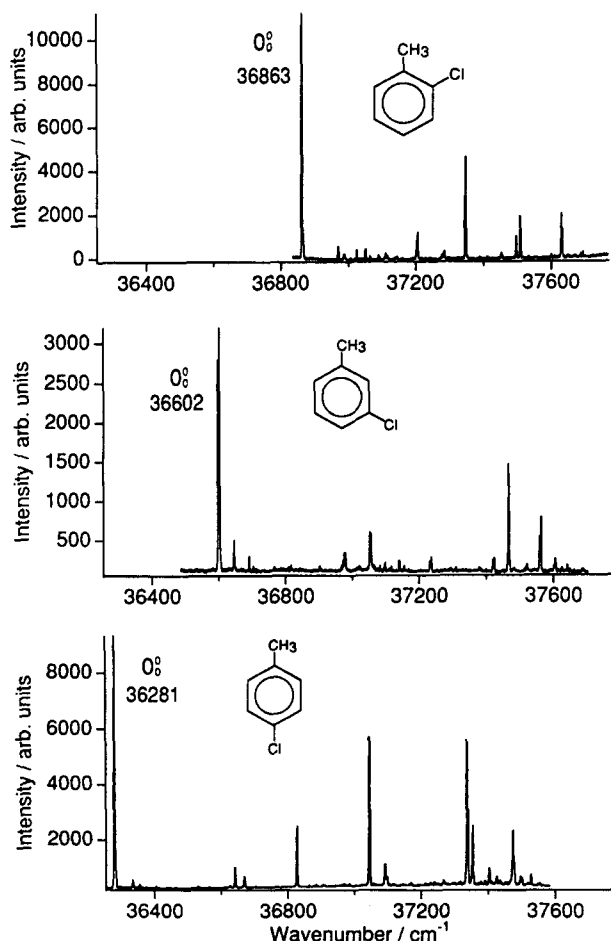


Fig. 1. Fluorescence excitation spectra of jet-cooled *o*-chlorotoluene (top), *m*-chlorotoluene (middle) and *p*-chlorotoluene (bottom). The origin ( $0_0^0$ ) of the spectrum is at  $36\,863 \text{ cm}^{-1}$  for *o*-chlorotoluene,  $36\,602 \text{ cm}^{-1}$  for *m*-chlorotoluene and  $36\,281 \text{ cm}^{-1}$  for *p*-chlorotoluene.

gas. The rotational temperature of the molecule in a supersonic free jet of 5 atm helium gas has been estimated to be less than 10 K and the vibrational temperature to be about 30 K [13]. For 3 atm helium gas, these temperatures may be slightly higher. The molecular beam was so cold that no hot vibrational bands could be observed at wavelengths longer than the 0–0 origin band. The strongest band observed in the excitation spectra shown in Fig. 1 was found to be the origin of the  $S_1$  state. The origin wavenumbers for *o*-, *m*- and *p*-chlorotoluene are  $36\,863 \text{ cm}^{-1}$ ,  $36\,602 \text{ cm}^{-1}$  and  $36\,281 \text{ cm}^{-1}$  respectively. The band observed at  $37\,467 \text{ cm}^{-1}$  in the spectrum of *m*-chlorotoluene [12] was found to be due to an impurity. Prominent bands, including the origin, observed in the spectrum of *m*-chlorotoluene in Fig. 1 are doublets whose lower frequency band is shifted by  $4.9 \text{ cm}^{-1}$ . A couple of weak bands can be observed in the wavenumber region from the origin to  $200 \text{ cm}^{-1}$  in the fluorescence spectra of *m*- and *p*-chlorotoluene. These bands are attributed to the methyl internal rotation which is discussed elsewhere [14]. Vibronic structures appear in the regions from 300 to  $1500 \text{ cm}^{-1}$  above the origin. In order to assign these bands, dispersed fluorescence spectra were taken by pumping each vibronic band observed in the excitation spectrum (Fig. 1).

The typical fluorescence spectra observed on excitation of the six bands of *p*-chlorotoluene are shown in Fig. 2. The excitation wavenumbers are indicated on the left side of the fluorescence spectra (the numbers in the spectra show the observed wavenumbers above the excitation transition, where the frequency scale is given by taking the transition energy to the vibrational 0 level of the  $S_0$  state as zero). Accordingly, the (0,0) excitation of the  $S_0$ – $S_1$  transition provides all of the vibrational frequencies in the  $S_0$  state. Excitation at  $36\,641 \text{ cm}^{-1}$  ( $(0,0) + 360 \text{ cm}^{-1}$ ) reveals a couple of vibronic bands; the strongest peak appears at  $368 \text{ cm}^{-1}$ , which corresponds to the vibrational frequency of the equivalent mode in the ground state ( $S_0$ ). The vibrational frequencies for *o*-, *m*- and *p*-chlorotoluene molecules in the  $S_0$  state have been given previously [15]. A comparison of the observed vibrational frequency in the dispersed fluorescence spectrum with the literature value enables the vibrational mode of the observed band in the excitation spectrum to be assigned. The  $368 \text{ cm}^{-1}$  band in Fig. 2(c) corresponds to the vibrational energy of the 7a mode in the ground state. In this paper, the vibrational mode is designated by the Wilson notation. Vibrational energy analyses of the dispersed fluorescence spectra, using the observed intensity patterns and IR and Raman frequencies [15], lead to the assignments of the fundamental bands in the excitation spectrum of each molecule (see Tables 1 and 2). In Fig. 2(f), a broad background spectrum can be observed, probably due to the occurrence of IVR processes. Furthermore, the band which appears at  $2195 \text{ cm}^{-1}$ , probably the second overtone of the  $1102 \text{ cm}^{-1}$  band, is surprisingly strong. However, the reason for this is not known.

Table 1 summarizes the vibrational frequencies of *p*-, *o*- and *m*-chlorotoluene in the  $S_1$  state and their assignments determined by the above measurements, together with their



Table 2  
Fundamental frequencies of *p*-, *o*- and *m*-chlorotoluene

<i>p</i> -Chlorotoluene			<i>o</i> -Chlorotoluene			<i>m</i> -Chlorotoluene		
Mode	S <sub>1</sub>	S <sub>0</sub> <sup>a</sup>	Mode	S <sub>1</sub>	S <sub>0</sub> <sup>a</sup>	Mode	S <sub>1</sub>	S <sub>0</sub> <sup>a</sup>
			(a')			(a')		
15	249	254	6a	643, 655	678	15	374	387
7a	360	377	12	768	808	7b	378	416
16a	386	405	7a	341	445	6a	454	522
12	547	636	6b	483	533	1	635	683
6a	765	797	(a'')			6b	823	858
10a	812, 817	819	10a	109	247	12	964	1002
1	1056	1090	16b	422	437			
9a	1072	1176						
13	1194	1208						

<sup>a</sup> Values taken from Ref. [15].

The fundamental frequencies of *o*-, *m*- and *p*-chlorotoluene are summarized in Table 2. The 341 cm<sup>-1</sup> band of *o*-chlorotoluene in the S<sub>1</sub> state was assigned to the 7a<sup>1</sup> mode, although the observed vibrational frequency (377 cm<sup>-1</sup>) in the S<sub>0</sub> state differs from the literature value (445 cm<sup>-1</sup>) [15]. The main reason why this band was assigned to the 7a mode is that the isotope shift of the 341 cm<sup>-1</sup> band is the largest [18]. In view of the isotope shift, the 341 cm<sup>-1</sup> band may be regarded as the 15 mode in analogy with *p*- or *m*-chlorotoluene. However, the S<sub>0</sub> frequency of the 15 mode for *o*-chlorotoluene is not available in the literature, so that the assignment of the 15 mode is not possible. Furthermore, it is not known whether the 643 cm<sup>-1</sup> or 655 cm<sup>-1</sup> band is the 6a mode because of the low spectral resolution.

### 3.2. C–Cl vibrational mode

Of the vibrational modes appearing in the fluorescence spectra, the C–Cl symmetric stretching modes for *p*-, *m*- and *o*-chlorotoluene molecules are determined to have vibrational energies of 360 cm<sup>-1</sup>, 378 cm<sup>-1</sup> and 341 cm<sup>-1</sup> in the S<sub>1</sub> state respectively. In comparison with the reported vibrational frequencies of the C–Cl stretching mode of *p*-dichlorobenzene (301 cm<sup>-1</sup>) [19,20] and 2,6-dichlorotoluene (342.2 cm<sup>-1</sup>) [21], these values are slightly higher. The value of 341 cm<sup>-1</sup> for the 7a mode of *o*-chlorotoluene is in excellent agreement with that of 2,6-dichlorotoluene, revealing that the additional chlorine substitution in *o*-chlorotoluene does not have any effect on the C–Cl vibrational frequency in the S<sub>1</sub> state.

The C–Cl stretching mode is very sensitive to the chlorine atom isotope, and the greatest isotope shifts for the various vibrational modes of *p*-dichlorobenzene have been observed by Rohlffing and Rohlffing [19] by the RE2PI technique. The same method has been applied to chlorotoluene molecules [18]. The 7a mode assigned to *o*-chlorotoluene in this study shows the largest isotope shift (2.9 cm<sup>-1</sup>) of the vibrational modes, while the isotope shifts of the 7a mode of *p*-chloro-

toluene and the 7b mode of *m*-chlorotoluene are 0.27 cm<sup>-1</sup> and 1.4 cm<sup>-1</sup> respectively, both smaller than those of the 15 mode vibrations (1.64 cm<sup>-1</sup> and 3.40 cm<sup>-1</sup> respectively). The isotope shift can be estimated from the ab initio calculation of the vibrational frequencies and normal modes, which was successfully demonstrated by Rohlffing and Rohlffing [19]. The same calculation will be carried out in the near future for chlorotoluene.

Also of interest is the observation that the stretching 7a mode of heavy chlorine in the molecule does not have the lowest frequency. The 15 mode vibration of *p*-chlorotoluene is about 110 cm<sup>-1</sup> lower than that of the 7a mode, as is the 15 mode of *m*-chlorotoluene, although the frequency difference is small. Furthermore, the characteristic feature of the C–Cl vibrational modes in Fig. 1 is the low emission intensity. The relative intensity estimated from the peak area and the laser intensity was normalized by an absorption cross-section obtained from RE2PI results [18]. These relative emission intensities obtained for each vibrational band reflect the non-radiative decay rate. The intensity of the 15 mode vibration is lower than that of the 6a mode in *m*- and *p*-chlorotoluene molecules. This indicates the possibility of mode selectivity in the photochemical dynamics of chlorotoluene molecules. Detailed analyses are now under way and will be published in the near future.

### References

- [1] T. Ichimura and Y. Mori, *J. Chem. Phys.*, 58 (1973) 288.
- [2] T. Ichimura, T. Hikida and Y. Mori, *J. Chem. Phys.*, 63 (1975) 1445.
- [3] A. Shimoda, T. Hikida, T. Ichimura and Y. Mori, *Chem. Lett.*, (1979) 265.
- [4] T. Ichimura, Y. Kohso, T. Hikida and Y. Mori, *J. Photochem.*, 26 (1984) 17.
- [5] T. Ichimura, N. Nahara, Y. Mori, M. Sumitani and K. Yoshihara, *Chem. Phys.*, 95 (1985) 9.
- [6] T. Ichimura, N. Nahara and Y. Mori, *Chem. Phys.*, 96 (1985) 453.
- [7] T. Ichimura, Y. Mori, H. Shinohara and N. Nishi, *Chem. Phys. Lett.*, 122 (1985) 51.

- [8] T. Ichimura, Y. Mori, H. Shinohara and N. Nishi, *Chem. Phys. Lett.*, 122 (1985) 55.
- [9] T. Ichimura, Y. Mori, H. Shinohara and N. Nishi, *Chem. Phys. Lett.*, 125 (1986) 263.
- [10] T. Ichimura, Y. Mori, H. Shinohara and N. Nishi, *J. Spectrosc. Soc. Jpn.*, 35 (1986) 299.
- [11] T. Ichimura, Y. Mori, H. Shinohara and N. Nishi, *Chem. Phys.*, 189 (1994) 117.
- [12] T. Ichimura, A. Kawana, T. Suzuki, T. Ebata and N. Mikami, *J. Photochem. Photobiol. A: Chem.*, 80 (1994) 145.
- [13] N. Mikami, A. Hiraya, I. Fujiwara and M. Ito, *Chem. Phys. Lett.*, 74 (1980) 531.
- [14] H. Kojima, T. Suzuki, T. Ichimura, A. Fujii, T. Ebata and N. Mikami, in preparation.
- [15] G. Varsanyi, *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*, Vol. 1, Adam Hilger, London, 1974.
- [16] I. Suzuka, N. Mikami and M. Ito, *J. Mol. Spectrosc.*, 52 (1974) 21.
- [17] M. Fukushima and K. Obi, *J. Chem. Phys.*, 96 (1992) 4224.
- [18] T. Ichimura, H. Shinohara, F. Misaizu, K. Ohashi and N. Nishi, *Int. Conf. on Photochemistry, I-30, Paris, 1991*, in preparation.
- [19] E.A. Rohlfing and C.M. Rohlfing, *J. Phys. Chem.*, 93 (1989) 94.
- [20] W.D. Sands and R. Moore, *J. Phys. Chem.*, 93 (1989) 101.
- [21] D.M. Lubman, R. Tembreull and C.H. Sin, *Anal. Chem.*, 57 (1985) 1084.