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Methyl Internal Rotation of Photoexcited Chlorotoluene Molecules

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Laser-induced fluorescence excitation and dispersed fluorescence spectra of jet-cooled chlorotoluene molecules were measured. Weak bands were observed near the origin for *p*- and *m*-chlorotoluene, and assigned to be the internal rotation of the methyl group in the S_0 and S_1 states. Internal rotational levels observed in the spectra were well reproduced by periodic potential with a free rotor basis set. The potential barrier heights for the S_0 and S_1 states of *p*-chlorotoluene are quite low, suggesting that the methyl rotor is almost free in both states. When *m*-chlorotoluene changes from the S_0 to the S_1 states, the potential barrier height increases, revealing that the methyl rotor is hindered in the S_1 state. For *o*-chlorotoluene, no internal rotational bands were observed, probably because of the large steric hindrance and/or the electronic properties of the Cl substituent. The contribution of the methyl internal rotation to the nonradiative processes is discussed using a comparison between the observed intensities and the Franck−Condon factors.

Introduction

The methyl internal rotation on toluene derivatives has been extensively studied by many researchers since Okuyama et al. applied the supersonic free jet technique to fluorotoluene molecules.[1−6] The fluorescence excitation and the dispersed fluorescence spectra of fluorotoluenes were observed and the low-frequency bands were assigned to the internal rotational bands in the first excited singlet (S_1) state and the ground (S_0) state for the first time.[1] They determined the potential curves of the internal rotational motion both in the S_0 and S_1 states from an analysis based on a one-dimensional free rotor basis set. Some studies on ab initio calculation have determined the methyl internal rotational potentials of toluene derivatives.[3,4] The relative geometry of an additional substituent in a toluene derivative plays an important role for the internal rotational motion in the S_0 state, whereas the motion is very sensitive to the electronic character in the S_1 state. The methyl internal rotational potential, however, is not well understood in the electronic excited states. Recently, an interesting suggestion in terms of the connection between the electronic character and the methyl internal rotational potential was provided by Fujii et al.[5] They indicated that the electronic properties of the electron-withdrawing or -donating substituent should play an important role for the methyl internal rotational potentials in the excited state. The investigation of the chlorotoluene molecule the substituent of which is an electron-donating Cl atom helps us to understand the methyl internal rotational potentials. The comparison between chlorotoluenes and other toluene derivatives should also interpret the effects on electronic properties.

On the other hand, Parmenter et al. suggested the methyl rotors as an accelerating functional group for intramolecular vibrational energy redistribution (IVR).[6] Mode selectivity of the internal rotation in the intersystem crossing (ISC) was postulated for methylglyoxal.[7] These results supply much motivation to study the methyl internal rotation for chlorotoluenes, because the Cl substituent should induce large spin−orbit interaction.[8] Photofragment spectroscopy on chlorinated benzene derivatives suggested that introduction of the methyl group to chlorobenzene also accelerates the ISC rate.[9] The photochemical dynamics of the chlorotoluene molecules should require the investigation of the methyl internal rotation. In a preliminary paper, we reported that laser-induced fluorescence technique can be applied to jet-cooled chlorotoluene molecules.[10] In this paper, extensive study of S_1 chlorotoluene molecules is presented in view of the internal rotation of the methyl group. Internal rotational bands observed for *p*- and *m*-chlorotoluene were assigned. Potential curves for the internal rotation of these molecules in the S_0 and S_1 states were determined. In addition, nonradiative processes from the internal rotation are discussed.

Experimental Section

Apparatus for the laser-induced fluorescence measurements is described briefly. Neon gas (2 atm) was passed through the sample reservoir heated at 310−350 K to maintain appropriate vapor pressure of chlorotoluene (about 10−90 Torr). The mixed gas was expanded into a 4 in. crossed chamber through a pulsed nozzle (General Valve) with a 500 μm diameter orifice. The expansion chamber was evacuated by a 6 in. oil diffusion pump with a water baffle and a mechanical rotary pump. The backing pressure in the expansion chamber was about $5-20 \times 10^{-5}$ Torr during a run at a repetition rate of 10 Hz, and was approximately 10^{-6} Torr without a run.

A dye laser (Molectron DL-223) was pumped with the third harmonic of a Nd:YAG laser (Quantel-Brilliant ω, 355 nm, ∼70 mJ/pulse) which was triggered externally by a pulse generator with an appropriate delay after the valve opening. The dye laser output (552−530 nm) was frequency doubled by an angle-tuned second harmonic crystal (BBO) and the fundamental light was removed with a filter (Toshiba UV-D33S). Coumarin 153 in methanol or methanol/1,4-dioxane was used for the dye laser. The spectral resolution was approximately 1 cm^{-1}.

The exciting laser light generated as described above was introduced into the expansion chamber with $X/D = 25$. Fluorescence from the supersonic free jet was observed by a

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photomultiplier tube (Hamamatsu 1P28) from a direction perpendicular to both the exciting light and the supersonic free jet. Dispersed fluorescence spectra were measured by a Nalumi 0.75 m monochromator with 0.1 mm slit width and spectral resolution was approximately 10 cm^{-1}. Signals from the photomultiplier tube were averaged by a boxcar integrator (Stanford SR250), digitized by an A/D converter, and then transferred to a personal computer. The laser intensity was simultaneously monitored with a photodiode to normalize the signal intensity.

Samples of *o*-, *m*-, and *p*-chlorotoluenes were purchased from Tokyo Kasei Co. *m*-Chlorotoluene was purified by distillation in a vacuum.

Analytical Treatment. The potential curves were determined using the assumption that the methyl top and the benzene framework are rigid. The wave function $\Psi(\phi)$ for the internal rotation should satisfy the following equation,

$$\left[-B\frac{\partial^2}{\partial\phi^2} + V(\phi)\right]\Psi(\phi) = E\Psi(\phi) \qquad (1)$$

where ϕ is the torsional angle between the methyl group and the benzene ring. B is the reduced rotational constant of the methyl rotor about the methyl top axis. In *o*- and *m*-chlorotoluenes, the potential $V(\phi)$ is expressed as follows:

$$V(\phi) = \frac{1}{2}\{V_3(1 - \cos 3\phi) + V_6(1 - \cos 6\phi)\} \qquad (2)$$

where V_3 and V_6 are potential barrier heights. In *p*-chlorotoluene, because of the higher symmetry, the potential $V(\phi)$ is expressed as

$$V(\phi) = \frac{1}{2}V_6(1 - \cos 6\phi) \qquad (3)$$

The wave function is expanded by a free rotor basis set. Here, a 25 function basis set is used for the calculation in analogy to the fluorotoluene molecules.[1] Eigenvalues are obtained by reproducing all observed internal rotational levels with B, V_3, and V_6 values as fitting parameters.

When the three parameters are used, the Franck−Condon overlap between the S_0 and S_1 states can be calculated. Relative intensity distributions of the internal rotational bands in the fluorescence excitation spectra and the dispersed fluorescence spectra are obtained by the Franck−Condon overlap calculation. The relative position of the methyl group between the S_0 and the S_1 states, which is indicated by the displacement angle α, is determined with the Franck−Condon overlap calculation. The Franck−Condon factor F is expressed by

$$F = |\langle\Psi_f(\phi + \alpha)|\Psi_i(\phi)\rangle|^2 \qquad (4)$$

Internal rotational energy levels are denoted by a combination of the rotational quantum number m of a one-dimensional free rotor and the symmetry species of the permutation inversion group. The levels are denoted as $0a_1$, $1e$, $2e$, $3a_1$, $3a_2$, $4e$, and so on in *o*- and *m*-chlorotoluenes, which belong to the G_6 permutation inversion group.[11] The levels are denoted as $0a_1'$, $1e''$, $2e'$, $3a_1''$, $3a_2''$, $4e'$, and so on in *p*-chlorotoluene, which belongs to the G_{12} permutation inversion group.[11] According to the selection rule, $a_1 \Leftrightarrow a_1$, $a_2 \Leftrightarrow a_2$, and $e \Leftrightarrow e$ transitions are allowed for *o*- and *m*-chlorotoluene, whereas $a_1' \Leftrightarrow a_1'$, $a_2' \Leftrightarrow a_2'$, $e' \Leftrightarrow e'$, $a_1'' \Leftrightarrow a_1''$, $a_2'' \Leftrightarrow a_2''$, and $e'' \Leftrightarrow e''$ transitions are allowed for *p*-chlorotoluene. The forbidden bands such as $a_1 \Leftrightarrow a_2$ and $e'' \Leftrightarrow e'$ weakly appear by Coriolis coupling between the internal rotation and the rotation of the whole molecule.

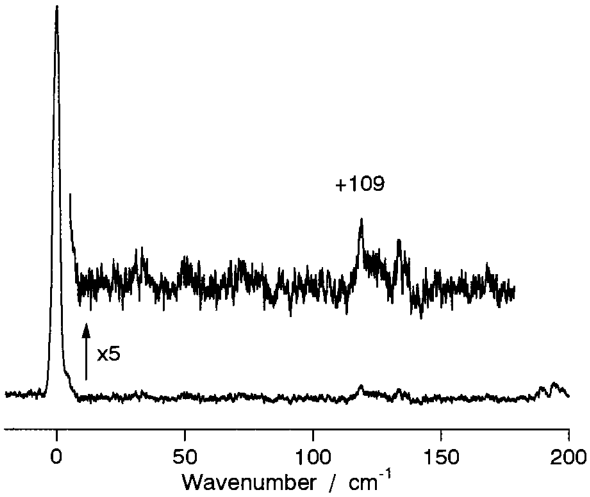

Figure 1. FE spectrum of the $S_1 \Leftarrow S_0$ transition for jet-cooled *o*-chlorotoluene near the origin. The jet expansion is with 2 atm Ne carrier gas. The origin band is at 36 863 cm^{-1}. The spectral resolution is approximately 1 cm^{-1}. Only a weak band was observed except for the origin band. The band displacement from the origin is given above the band. The band should be assigned to the 10a mode. See text for details. The scale shows frequencies (cm^{-1}) from the origin.

Results and Discussion

Internal Rotational Band Assignments. A substituted toluene derivative usually exhibits low-frequency bands because of the methyl internal rotation. Figure 1 shows the fluorescence excitation (FE) spectrum of *o*-chlorotoluene in a supersonic free jet near the origin (36 863 cm^{-1}). No band was found up to 100 cm^{-1} above the origin. Figure 2a shows the dispersed fluorescence (DF) spectrum of *o*-chlorotoluene obtained by pumping the origin of the S_1 state. No band was found up to 200 cm^{-1} above the pumping position. The DF spectrum obtained by pumping the 109 cm^{-1} band is shown in Figure 2b, where a band at 252 cm^{-1} was observed. Richard et al. assigned the 109 cm^{-1} band as $3a_1$ in the S_1 state.[4] Instead, this band should be the vibronic band, $10a_0^1$, because the energy of 252 cm^{-1} band observed in Figure 2b is close to the value of 246 cm^{-1} for the 10a mode in the S_0 state.[12] Hence, this band must not be an internal rotation. The reason for the lack of the internal rotational bands will be discussed in the following section. Figure 3 exhibits the FE spectrum of *p*-chlorotoluene observed near the origin (36 281 cm^{-1}). The origin band provides a single peak, consisting of the two components that are due to the transitions, $0a_1'(S_1) \Leftarrow 0a_1'(S_0)$ and $1e''(S_1) \Leftarrow 1e''(S_0)$. Because the energy difference between the $0a_1$and $1e$ levels for the internal rotation in the S_0 state is generally quite small, the molecules even in a supersonic jet are populated in their levels because of the different nuclear spins. Therefore, internal rotational bands were assigned as transitions originating from these initial levels of $0a_1'$ and $1e''$ in the S_0 state. The reason for the single peak is that the energy difference between the transitions should be less than 1 cm^{-1}. The low-frequency band structure in *p*-chlorotoluene was assigned in comparison with the *p*-fluorotoluene spectrum,[1] the profiles of which resemble each other. Table 1 lists the observed energies from the origin. Although the transitions of $3a_1''(S_1) \Leftarrow 0a_1'(S_0)$ and $4e'(S_1) \Leftarrow 1e''(S_0)$ are forbidden by the selection rule, the weak bands barely appear owing to the interaction between the internal

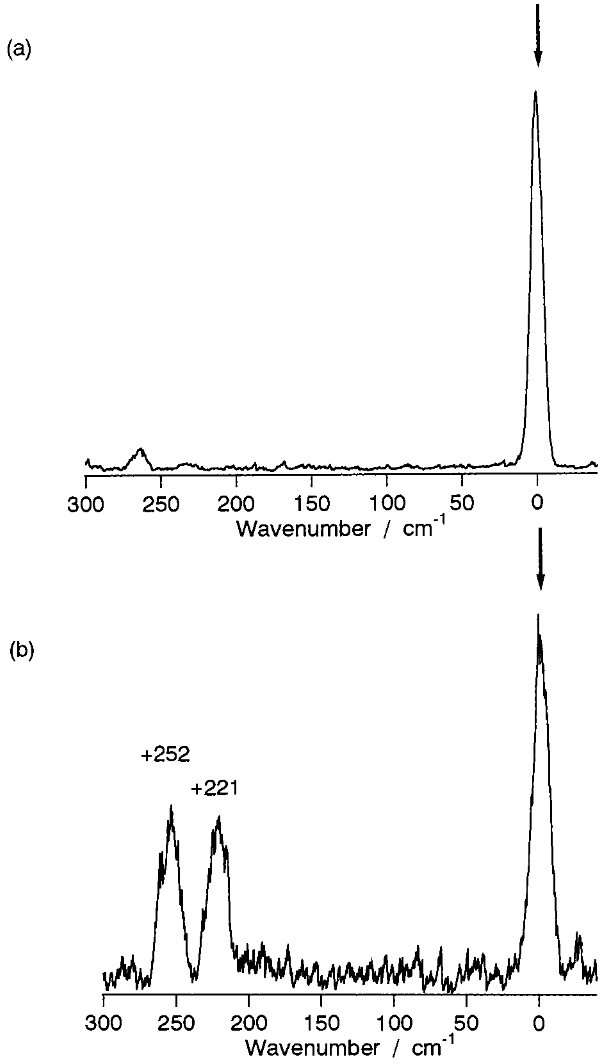

Figure 2. DF spectra of the $S_1 \rightarrow S_0$ transition for jet-cooled *o*-chlorotoluene observed by pumping the origin (a) and 109 cm^{-1} band (b) observed in Figure 1. The scale shows frequencies (cm^{-1}) from the pumping positions. The spectra are aligned by the positions. The positions are indicated by arrows. The spectral resolution is approximately 10 cm^{-1}. No band was observed in the region of 0−200 cm^{-1} except for the origin band in (a). Two bands appeared except for the band at the pumping position in (b). The band displacements from the pumping position are given above the bands. The stronger 252 cm^{-1} band should be assigned to the 10a mode.

rotation and the rotation of the whole molecule. To confirm the assignments in the S_1 state and to obtain the internal rotational levels in the S_0 state, the DF spectra of *p*-chlorotoluene were observed by pumping the $0a_1'$ and $1e''$ (a), $3a_1''$ (b), and $4e'$ (c) levels in the S_1 state (Figure 4). These spectra are drawn with the same horizontal scale and are adjusted to align with the excitation positions, which are indicated by arrows in Figure 4. According to the selection rule, the observed bands can be assigned as shown in the figure, and are summarized in Table 1. All of the bands in the spectra obtained by pumping the $0a_1'$ and $3a_1''$ levels in the S_1 state are assigned to the levels of a_1' and a_1'' symmetry, and those obtained by pumping the $1e''$ and $4e'$ levels are assigned to e' and e'' symmetry.

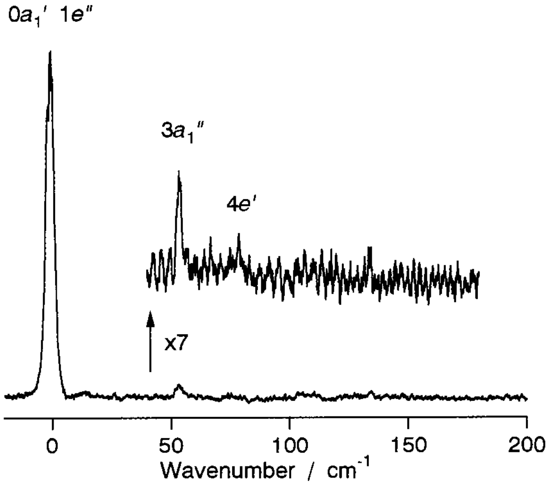

Figure 3. The FE spectrum of the $S_1 \leftarrow S_0$ transition for jet-cooled *p*-chlorotoluene near the origin. The origin band is at 36 281 cm^{-1}. Two weak bands were observed and assigned to the internal rotation. The single origin was due to small energy difference between the $0a_1$ (S_1) $\leftarrow$ $0a1$ (S_0) and $1e$ (S_1) $\leftarrow$ $1e$ (S_0) transitions. The scale shows frequencies (cm^{-1}) from the origin. Assignments are indicated above each band.

TABLE 1: Internal Rotational Levels for the Methyl Group of *p*-Chlorotoluene in the S_0 and S_1 States

	S_0 state (cm^{-1})		S_1 State (cm^{-1})	
species	obsd.[a]	calcd.[a,b]	obsd.[a]	calcd.[a,c]
$0a_1'$	0	0	0	0
$1e''$	0	0	0	0
$2e'$		16		14
$3a_2''$		45		41
$3a_1''$	53	53	55	54
$4e'$	80	81	75	76
$5e''$	114	130		120
$6a_2'$		189		172
$6a_1'$	195	195		179

[a] All e' and e'' species levels are relative to the $1e''$ level. [b] S_0 state: $B = 5.40$ cm^{-1}, $V_6 = -17$ cm^{-1}. [c] S_1 state: $B = 4.91$ cm^{-1}, $V_6 = -38$ cm^{-1}.

To obtain the potential curves for the internal rotation of the S_0 and S_1 states, each level energy was determined to reproduce the experimental results with the parameters, B and V_6. The best fitting results were obtained with $B = 5.40$ cm^{-1} and $V_6 = -17$ cm^{-1} for the S_0 state and $B = 4.91$ cm^{-1} and $V_6 = -38$ cm^{-1} for the S_1 state. Table 1 also lists the calculated level energies. They are in good agreement with the observed values. Figure 5a shows the FE spectrum of *m*-chlorotoluene in the wavenumber region of 36 500−38 300 cm^{-1}, and Figure 5b is the expanded spectrum up to 150 cm^{-1} in Figure 5a. The strongest band observed at 36 602 cm^{-1} is assigned to the S_1 origin. Vibronic structure appears in the region above 150 cm^{-1} from the origin. These bands were already assigned from measurements of the DF spectra.[10] The prominent bands including the origin observed in the figure are doublets the lower frequency bands of which are shifted by 4 cm^{-1}. These bands are assigned to the internal rotational bands of the methyl group in the S_1 state. Doublets of prominent vibronic bands are attributed to two origins of the internal rotation, because of $0a_1$ (S_1) $\leftarrow$ $0a_1$ (S_0), and $1e$ (S_1) $\leftarrow$ $1e$ (S_0) transitions. Accordingly, the internal rotational bands were assigned in a manner analogous to that of *p*-chlorotoluene. The assignments are also indicated in Figure 5b. The assignments and observed energies are listed in Table 2. Bands resulting from $a_1 \leftrightarrow a_2$ transitions are too weak to be observed owing to the forbidden transition.

Figure 6 shows DF spectra of *m*-chlorotoluene observed with pumping the $0a_1$ (a) and $1e$ (b) levels in the S_1 state, respectively. According to the selection rule, all bands observed in the $0a_1$ excitation are assigned to the levels of a_1 symmetry and those in the $1e$ excitation are assigned e symmetry. The band

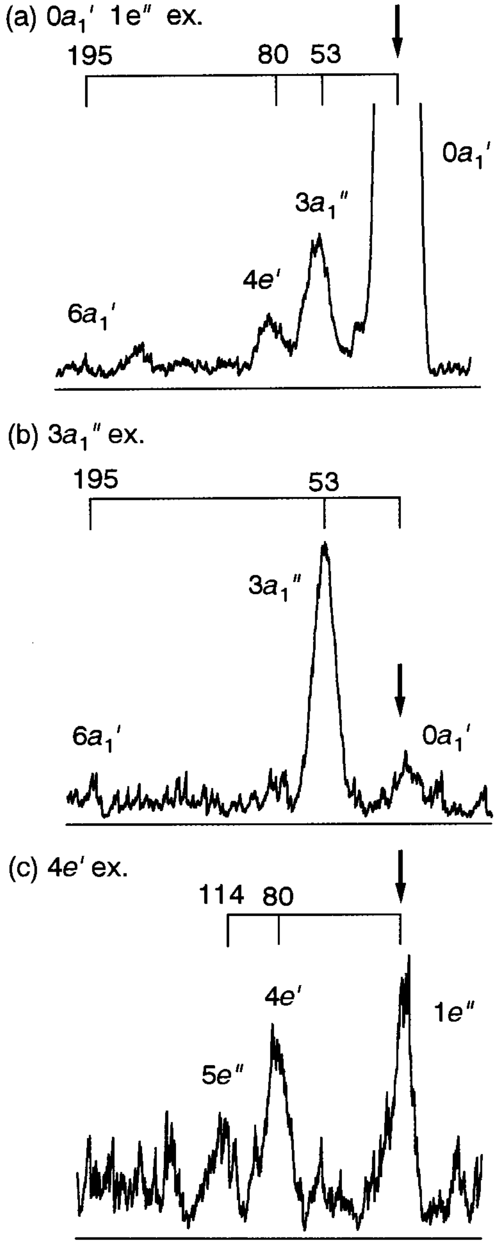

Figure 4. DF spectra of the $S_1 \Rightarrow S_0$ transition for jet-cooled *p*-chlorotoluene obtained by pumping the $0a_1'$ and $1e''$ (a), $3a_1'$ (b), or $4e'$ (c) bands observed in Figure 3. The spectra are aligned by the pumping positions. The scale shows band displacements (cm^{-1}) from the pumping positions. According to the selection rule, all the bands observed in (b) were assigned to the a_1' and a_1'' species in the S_0 state and all the bands in (c) were assigned to the e' and e'' species. All symmetry species appeared in (a) because of simultaneous pumping of the $0a_1'$ and $1e''$ bands, the spacing of which is almost equal. The peak intensity for the $1e''$ band in (c) included the scattered light. The assignments are indicated above each band. Pumping positions are indicated by arrows.

assignments are also indicated in Figure 6. Table 2 contains a listing of energies from the origins for the internal rotation.

Potential curves for the internal rotation of *m*-chlorotoluene were obtained in the same manner as those for *p*-chlorotoluene. The best fits were obtained with $B = 5.32$ cm^{-1}, $V_3 = 1$ cm^{-1}, and $V_6 = -8$ cm^{-1} for the S_0 state, and $B = 4.15$ cm^{-1}, $V_3 = 129$ cm^{-1}, and $V_6 = -39$ cm^{-1} for the S_1 state. The calculated level energies are listed in Table 2 together with the observed level energies. The good agreement strongly suggests the validity of the assignments.

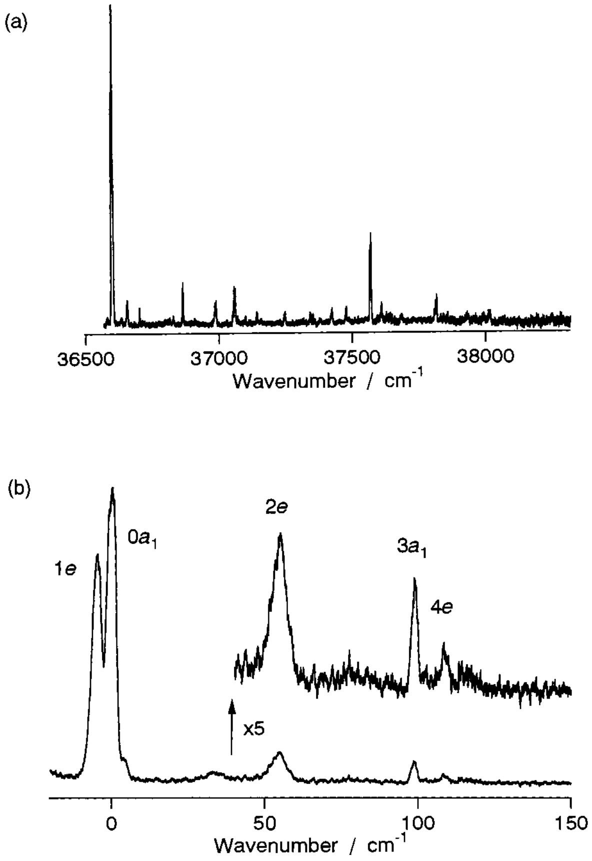

Figure 5. (a) FE spectrum of the $S_1 \Leftarrow S_0$ transition for jet-cooled *m*-chlorotoluene in the wavenumber region of 36 500−38 300 cm^{-1}. The origin band is at 36 602 cm^{-1}. The prominent vibronic bands were observed, and the internal rotational bands appeared to accompany the origin and some vibronic bands in the spectrum. (b) The expanded spectrum near the origin. A couple of weak bands for the internal rotation appeared and the assignments are indicated above each band. The horizontal scale shows frequencies (cm^{-1}) from the $0a_1$ (S_1) $\Leftarrow$ $0a_1$ (S_0) band.

TABLE 2: Internal Rotational Levels for the Methyl Group of *m*-Chlorotoluene in the S_0 and S_1 States

	S_0 state (cm^{-1})		S_1 state (cm^{-1})	
species	obsd.[a]	calcd.[a,b]	obsd.[a]	calcd.[a,c]
$0a_1$	0	0	0	0
$1e$	0	0	−4	−4
$2e$	15	16	53	53
$3a_2$		43		52
$3a_1$	50	50	89	89
$4e$	80	80	110	110
$5e$	126	128		149
$6a_2$		186		183
$6a_1$	193	192		185

[a] All *e* species levels are relative to the 1*e* level. [b] S_0 state: $B = 5.32$ cm^{-1}, $V_3 = 1$ cm^{-1}, $V_6 = -8$ cm^{-1}. [c] S_1 state: $B = 4.15$ cm^{-1}, $V_3 = 129$ cm^{-1}, $V_6 = -39$ cm^{-1}.

Potential Curves for the Methyl Internal Rotation. Franck−Condon factors for *m*-chlorotoluene were calculated by using values of *B*, V_3, and V_6 obtained in the previous section. Figure 7 shows the calculated values (open bars) for $\alpha = 60°$ and observed (solid bars) intensity distribution of internal rotational bands for the FE spectrum (a) and DF spectra (b) of *m*-chlorotoluene, respectively. The calculation at $\alpha = 60°$ well reproduced the intensity distributions obtained by the DF spectra, although the intensities of the $3a_1$ and $4e$ bands in the FE spectrum were much weaker than those calculated. The calculated intensity distributions for the $S_1 \Leftarrow S_0$ transition do

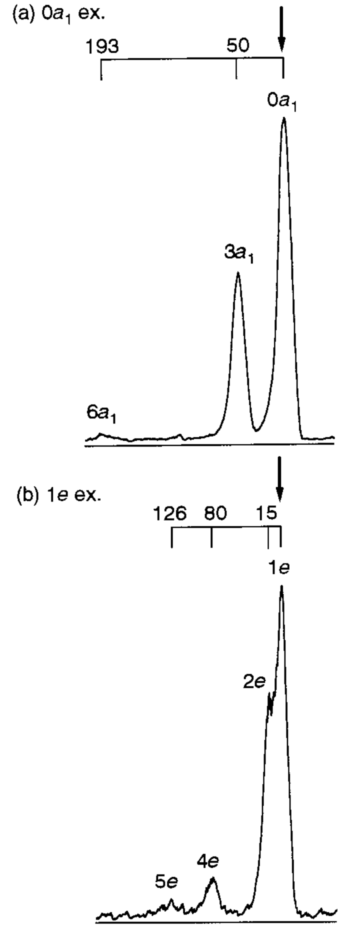

Figure 6. DF spectra of the $S_1 \Rightarrow S_0$ transition for jet-cooled *m*-chlorotoluene obtained by pumping the $0a_1$ (a) or $1e$ (b) bands observed in Figure 5b. The spectra are aligned by the pumping positions. The scale shows band displacements (cm^{-1}) from the pumping positions. All the bands observed in (a) were assigned to the a_1 symmetry species in the S_0 state and all the bands in (b) were assigned to the e symmetry species. The assignments are indicated above each band. Pumping positions are indicated by arrows.

not agree with the observed intensity distributions, whereas those for the $S_1 \Rightarrow S_0$ transitions do agree (see Figure 7). In Figure 7a the relative intensities of the FE spectrum of the transitions above the $2e$ level are much less than calculated intensities for *m*-chlorotoluene. The relative fluorescence intensity of each band in the FE spectrum should reflect the relative fluorescence quantum yield of each band. Accordingly, the decrease of the relative fluorescence intensities postulates that the internal rotation should influence the nonradiative processes. This is discussed in detail, including resonant-enhanced two-photon ionization spectra, elsewhere.[13]

The Franck–Condon factors could not be calculated for *p*-chlorotoluene because most of the observed bands are forbidden transitions. It is not a serious problem to determine the displacement between the S_0 and S_1 states. The potential function of this molecule is of purely 6-fold axis symmetry (60° period).

When the values of V_3, V_6, and α are used, the potential curves for the internal rotation in both the S_0 and S_1 states can be drawn. Figure 8 illustrates the potential curves and the internal rotational levels in the S_0 and S_1 states for *m*-chlorotoluene (a) and *p*-chlorotoluene (b), respectively. For both *m*- and *p*-chlorotoluenes, the potential barrier heights were found to be extremely low in their S_0 states. The low heights were also obtained by ab initio calculation.[3] The methyl group becomes almost a free rotor in the S_0 states. The result suggests that the geometry of the molecule plays an important role for the internal rotational motion in the S_0 state. The low barrier height in the S_0 state should be caused by the small steric hindrance between the Cl substituent and the methyl group set apart. The barrier heights, however, increase upon their S_1 states, although the increase for *p*-chlorotoluene is slight. The drastic increase for *m*-chlorotoluene means that the free rotation in the S_0 state should be greatly hindered in the S_1 state. The increase should reflect electronic properties of the electron-donating Cl substituent. The electronic properties of the CN substituent were discussed by Fujii et al.[5] In *m*-tolunitrile, the increment of the potential barrier height with the electronic excitation was quite small, and in *p*-tolunitrile, the height decreased. They concluded that the irregularity should result from the electronic properties of the CN substituent which is the electron-withdrawing group. The potentials for *m*- and *p*-chlorotoluene molecules are likely to be similar to other toluene derivatives the substituents of which are electron-donating groups.

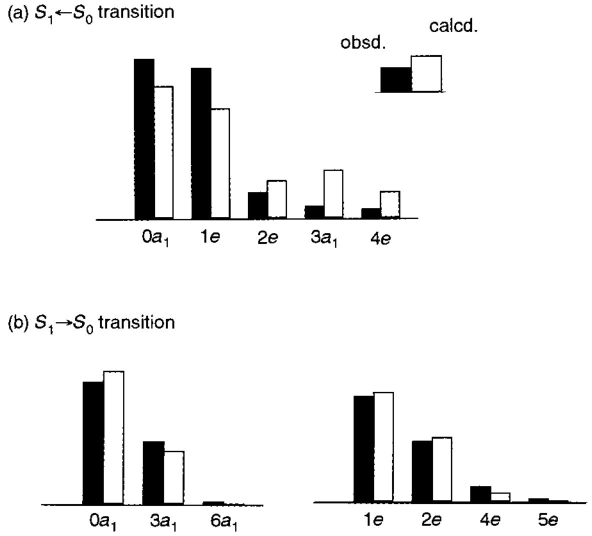

Figure 7. Comparisons between calculated Franck–Condon factors and observed intensity distributions of the internal rotation in the FE spectrum (a) and DF spectra (b) for *m*-chlorotoluene. Open bars are calculated values and solid bars are observed values. The observed values are in good agreement with the calculation in the $S_1 \Rightarrow S_0$ transition (b). The observed intensities are much weaker than the calculated intensities for the $3a_1$ and $4e$ levels in the $S_1 \Leftarrow S_0$ transition (a).

Generally, the barrier height of *o*-substituted toluene derivatives drastically decreases in going from the S_0 to the S_1 states, although the methyl internal rotation is quite hindered in the S_0 state. Such a tendency was explained in terms of the steric hindrance of the substituent to the methyl group, and the electronic properties of the substituent. In the S_0 state, the large barrier height should result from the great steric hindrance of a nearby substituent, whereas the cancellation of the height may be caused by the electronic properties of an electron-donating substituent in the S_1 state. The internal rotational bands must be observed in the spectra if the methyl internal rotational potentials for *o*-chlorotoluene are similar to the potentials described above. The lack of the bands in the spectra indicates that the potentials for *o*-chlorotoluene are quite different from those of other toluene derivatives. The lack should be observed if the potential curves in both the S_0 and S_1 states are very similar and hence it gives rise to very small Franck–Condon factors of the internal rotation. In fact, the internal rotational bands were not observed in the FE and DF spectra (see Figures 1 and

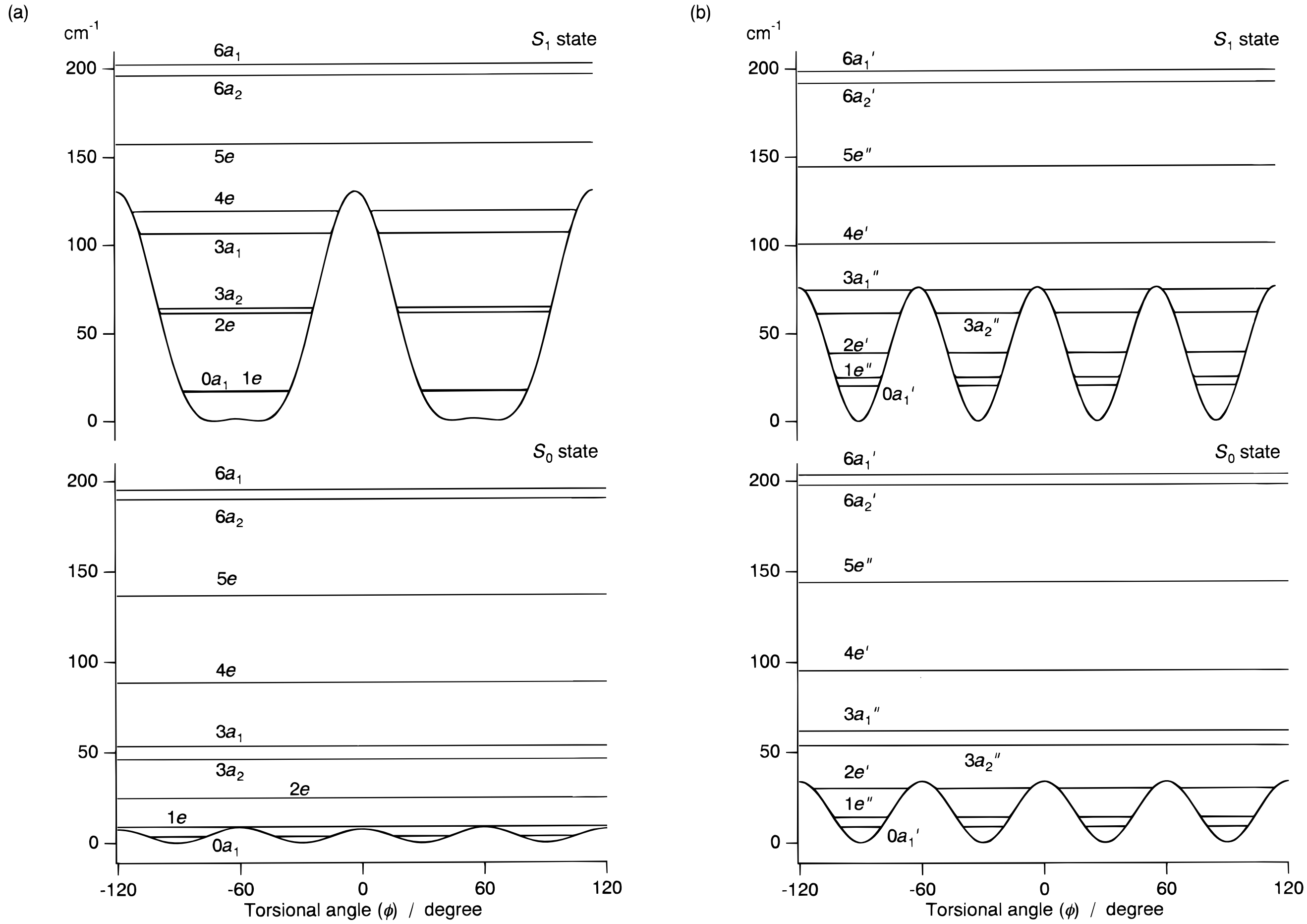

Figure 8. Potential curves and internal rotational levels in the S_0 and S_1 states for *m*-chlorotoluene (a) and *p*-chlorotoluene (b); $V_3 = 1$ cm^{-1}, $V_6 = -8$ cm^{-1}, $B = 5.32$ cm^{-1} in S_0 *m*-chlorotoluene; $V_3 = 129$ cm^{-1}, $V_6 = -39$ cm^{-1}, $B = 4.15$ cm^{-1} in S_1 *m*-chlorotoluene; $V_6 = -17$ cm^{-1}, $B = 5.40$ cm^{-1} in S_0 *p*-chlorotoluene; $V_6 = -38$ cm^{-1}, $B = 4.91$ cm^{-1} in S_1 *p*-chlorotoluene. The methyl rotor is almost free rotation in the S_0 state for both *m*- and *p*-chlorotoluenes. The internal rotation is greatly hindered in the S_1 state for *m*-chlorotoluene.

2). The similarity should be led by the large potential barrier heights in both states. The Cl substituent should be bulky enough even in the S_1 state. The internal rotational band was not observed for *o*-tolunitrile, for which a similar reason was also suggested.[5] The similarity indicates that the steric hindrance of the Cl substituent is quite large, such as the CN substituent, and/or the electronic properties of the Cl substituent have little effect in the S_1 state.

Conclusion

Laser-induced fluorescence spectra of jet-cooled chlorotoluenes in the S_1 state were observed. The methyl internal rotational bands observed for *p*- and *m*-chlorotoluene were assigned and their potentials were obtained. The potential barrier heights for the S_0 state of *m*- and *p*-chlorotoluene are quite low, suggesting that the methyl groups are almost free rotating. Changing from the S_0 to the S_1 states causes the potential barrier height to increase for both molecules. The increase should be due to the electronic properties of the electron-donating Cl substituent in the S_1 state. On the other hand, no internal rotational bands were observed in the FE and DF spectra for *o*-chlorotoluene. This is caused by small Franck−Condon overlap of the internal rotational bands. The potential curves of the internal rotation should be similar in both the S_0 and S_1 states. The reason should be explained by the large steric hindrance of the Cl substituent and/or the minor effect of the electronic properties of the electron-donating Cl substituent.

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References and Notes

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