Rotational Isomers and Internal Rotation of the CH_3 Group in S_0 , S_1 , and Ion of *o*-Cresol

Tomoko Aota, Takayuki Ebata, and Mitsuo Ito*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan (Received: September 21, 1988)

The fluorescence excitation, dispersed fluorescence, and two-color photoionization spectra have been measured for jet-cooled o-cresol. The cis and trans isomers were identified, and the potential energy curve of the internal rotation of the methyl group was determined in the S₀, S₁, and ionic states. The hindered methyl internal rotation in the S₀ state becomes an almost free rotation in the S₁ state, which becomes hindered again by an ionization. The results are compared with those of *m*-cresol.

Introduction

In ortho- or meta-substituted phenol, there exist two isomers, cis and trans, arising from an orientation of the OH group with respect to the substituent at the ortho or metha position. In a series of our work we have demonstrated that electronic spectroscopy combined with the supersonic expansion technique is a powerful tool to study the rotational isomerism of large polyatomic molecules, such as phenol derivatives.¹⁻⁶ In the course of the study, it was found that the interaction of the OH group with the substituent changes dramatically upon the electronic excitation.⁶ Especially, a methyl group as the substituent is very sensitive to such an interaction, and its internal rotational motion completely changes with a change in the electronic state. In a previous paper, we reported the rotational isomers of m-cresol and the internal rotation of the CH_3 group in S_0 , S_1 , and the ion. The cis and trans isomers of the neutral molecule and its ion were clearly identified. It was found for both isomers that a nearly free rotation of the CH_3 group in S₀ becomes a greatly hindered internal rotation by the electronic excitation and ionization, indicating a great enhancement of hyperconjugation in the latter states.

In the present study, we have studied the electronic spectra of jet-cooled o-cresol. In this molecule, a fairly large steric effect exists between the two adjacent substituents of CH_3 and OH. It is quite interesting to see how this steric effect influences the rotational isomerism and also the internal rotation of the CH₃ group, for S_0 , S_1 , and the ion. The fluorescence excitation spectrum of jet-cooled *o*-cresol due to the $S_1 \leftarrow S_0$ transition was already reported by Appel and Kleinermanns.⁷ They concluded that only the trans isomer exists in the S_0 state. In addition to the fluorescence excitation spectrum, we measured the dispersed fluorescence spectra and the two-color ionization spectra of the molecule and its hydrogen-bonded complexes. In contrast to the conclusion reported by Appel and Kleinermanns, the existence of both cis and trans isomers was definitely established. The characteristic difference in the internal rotation of the methyl group was also found between the two isomers in their S_0 , S_1 , and ionic states.

Experimental Section

The experimental setup for the measurement of the fluorescence excitation, dispersed fluorescence, and two-color ionization threshold spectra of jet-cooled molecule has been described elsewhere.⁶ o-Cresol was heated to 330 K in a nozzle chamber and seeded in 2 atm of He gas. In the case of producing a hydrogen-bonded molecule with water, diethyl ether, or *p*-dioxane, the solvent pressure was controlled by the use of a thermoregulator in which the solvent was immersed. The seeded gas mixture was expanded through a 400-µm-diameter nozzle.

The $S_1 \leftarrow S_0$ excitation was achieved by the frequency-doubled output of a tunable pulsed dye laser (Lambda Physik FL 2002) pumped by a XeCl excimer laser (Lambda Physik EMG 103). The fluorescence excitation spectrum of the jet-cooled molecule was measured by monitoring total fluorescence while scanning the laser wavelength. The fluorescence from the various vibronic levels in the S_1 state was dispersed by a Nalumi 0.75-m monochromator and detected by a photomultiplier (HTV R-928). The signal was amplified and then averaged by a boxcar integrator (Brookdeal 9415/9425) and recorded on a chart recorder.

In the two-color ionization threshold measurement, the output of the excimer laser was split by a beam splitter to excite two dye lasers. The first laser (ν_1) pumped the molecule from the S₀ state to the S₁ vibronic state and then the second laser (ν_2) excited the S₁ state molecule to the ionization threshold region. Ions were extracted to a subchamber and detected by a channel electron multiplier. The signal was amplified and processed by the boxcar integrator. In the study of the hydrogen-bonded complexes, extracted ions were mass analyzed by a quadrupole mass filter.

o-Cresol was purchased from Aldrich. The sample was of 99% purity and was used without purification. p-Dioxane (99% purity) and diethyl ether were purchased from Tokyo Kasei and degassed by freeze-pump-thaw cycles before use.

Results and Discussion

Figure 1 shows the fluorescence excitation spectrum of jetcooled *o*-cresol together with the vapor absorption spectrum at room temperature. In the jet-cooled spectrum, the bands at frequencies lower than 36 100 cm⁻¹ were identified to be due to the hydrogen-bonded complex of *o*-cresol formed with water contained as an impurity in the sample. The identification was performed by measuring the mass spectrum of the complex ion produced by 1 + 1 resonance-enhanced multiphoton ionization.

The next step is to distinguish bands belonging to the cis and trans isomers, if both isomers are present. Figure 2 shows the enlarged portion of the fluorescence excitation spectrum around the band origin. Between 36 200 and 36 300 cm⁻¹ there are several vibronic bands of medium intensity with irregular spacing, which are probably the vibronic bands due to the internal rotation of the methyl group. The peak at 36 421 cm⁻¹ is most intense, and there is another peak at 76 cm⁻¹ on the higher frequency side. In their spectroscopic study of jet-cooled o-cresol, Appel and Kleinermanns tentatively assigned the band at 36 205 cm⁻¹ as the band origin and the most intense 36 421-cm⁻¹ band (216 cm⁻¹ above the 36 205-cm⁻¹ band) as the vibronic band involving mode 11 in the S₁ state.⁷ They also concluded that all the bands in the excitation spectrum belong to the trans isomer and only the trans isomer exists in the ground state.

⁽¹⁾ Oikawa, A.; Abe, H.; Mikami, N.; Ito, M. J. Phys. Chem. 1983, 87, 5083.

⁽²⁾ Oikawa, A.; Abe, H.; Mikami, N.; Ito, M. J. Phys. Chem. 1984, 88, 5180.
(3) Oikawa, A.; Ito, M. J. Mol. Struct. 1985, 126, 133.

⁽⁴⁾ Oikawa, A.; Abe, H.; Mikami, N.; Ito, M. Chem. Phys. Lett. 1985, 120, 133.

 ⁽⁵⁾ Yamamoto, S.; Okuyama, K.; Mikami, N.; Ito, M. Chem. Phys. Lett.

^{1986, 125, 1.} (6) Mizuno, H.; Okuyama, K.; Ebata, T.; Ito, M. J. Phys. Chem. 1987,

^{91, 5589.} (7) Appel, L.; Kleinermanns, K. Ber, Bunsen-Ges, Phys. Chem. 1987, 91

⁽⁷⁾ Appel, I.; Kleinermanns, K. Ber. Bunsen-Ges. Phys. Chem. 1987, 91, 140.



Figure 1. (a) Absorption spectrum of *o*-cresol in the gas phase at room temperature. (b) Fluorescence excitation spectrum of jet-cooled *o*-cresol. The spectrum was measured at 15 mm downstream and is normalized by a laser power.



Figure 2. Fluorescence excitation spectrum of jet-cooled *o*-cresol around the band origin.

However, we have found that both isomers exist in the ground state. The following is the procedure to identify the isomers. Because the hydrogen atom of the OH group is very close to the methyl group in the cis isomer but not in the trans isomer, the capability to make the hydrogen-bonded complex with a proton-accepting molecule will be quite different between the isomers. The trans isomer will have a higher ability to make the complex than the cis isomer because steric hindrance is much smaller in the former isomer. Figure 3 shows the fluorescence excitation spectrum of o-cresol when the mixture of diethyl ether or p-dioxane vapor with He was used as a career gas. In the region around 35900 cm⁻¹, the peaks due to the hydrogen-bonded complex between o-cresol and diethyl ether or p-dioxane newly appear, while the bands in the 36200-36300-cm⁻¹ region disappear. However, the most intense band at 36 421 cm⁻¹ still exists strongly. There is a strong coincidence between the appearance of the bands due to the hydrogen-bonded complex and the disappearance of the bands in the 36 200- and 36 300-cm⁻¹ regions but not for the 36 421-cm⁻¹ peak. These results indicate that the group of the bands in the 36 200-36 300-cm⁻¹ region belongs to one of the isomers and the 36421-cm⁻¹ band belongs to another. From the point of view of the capability to make the hydrogen-bonded complex, we can conclude that the former bands belong to the trans isomer and the latter to the cis isomer.

Now we will determine the vibrational energy levels and potential energy curves of the internal rotation of the methyl group in both the S₀ and S₁ states. The low-frequency bands (0, 42, 74, and 97 cm⁻¹) associated with the band at 36 205 cm⁻¹ in the fluorescence excitation spectrum can be easily assigned to be the internal rotational levels of the trans isomer in S₁ from a close similarity in the spectral feature with the low-frequency bands of the CH₃ internal rotational levels of *o*-fluorotoluene.⁸ From



Figure 3. Fluorescence excitation spectra of (a) *o*-cresol-diethyl ether and (b) *o*-cresol-*p*-dioxane hydrogen-bonded complexes. All the bands below $36\,100 \text{ cm}^{-1}$ are assigned to be due to the complexes.



Figure 4. Dispersed fluorescence spectra measured after the excitation of individual bands of CH_3 internal rotational levels of trans and cis isomers of *o*-cresol.

the similarity, tentative assignments of the individual low-frequency bands are made as given in Figure 2. For the cis isomer the intense peak at 36 421 cm⁻¹ can be assigned to be the band origin. The band at 76 cm⁻¹ above the origin is assigned to be the $3a_1$ internal vibrational level of the S_1 state.

These assignments are further confirmed by measuring the dispersed fluorescence spectra. The assignment is based on the symmetry selection rules "a₁" \leftrightarrow "a₁" and "e" \leftrightarrow "e". Figure 4 shows the dispersed fluorescence spectra obtained by exciting the individual internal rotational bands of the trans (Figure 4a) and cis (Figure 4b) isomer. In the trans isomer, the fluorescence spectrum obtained by exciting the band origin (36 205 cm⁻¹) consists of the transitions from the 0a₁ and 1e levels in S₁ as evidenced by the appearance of both a₁ and e levels in S₀. The fluorescence spectrum obtained by the 2e and 4e levels give identical levels having "e" symmetry of the S₀ state. In the cis isomer fluorescence spectrum obtained by the excitation of the band origin shows 3a₁ and 4e vibrational levels that are degenerated in the S₀ state. The fluorescence spectrum from the 3a₁ level gives a set of "a₁" vibrational levels in the S₀ state.

The observed energy levels for the internal rotation of the methyl group are used to calculate the potential energy curves for this motion. The procedure of the calculation can be found in previous papers.^{6,8} The potential function $V(\varphi)$ is assumed by

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

TABLE I: Energy Levels (cm^{-1}) of the Internal Rotation of the Methyl Group of *trans-o*-Cresol in the S₀, S₁, and Ionic States

		S ₀		S_1^a		ion ^b		
spe	cies	obsd	calcd ^c	obsd	calcd ^d	obsd	calcde	
0	a1	0	0	0	0	0	0	
1	e	0	0	0	1.3		0	
2	e	118	114	42	41		117	
3	a,	213	210	74	73	221	221	
4	e.	213	216	92	98	242	224	
5	e	283	285		143		307	
6	a1	340	339		201	364	364	
7	e	381	391		266		404	

^a The zero-point energy is 36 205 cm⁻¹. ^b The ionization potential is 66 758 cm⁻¹. ^c $V_3 = 355$ cm⁻¹; $V_6 = -7$ cm⁻¹; B = 5.295 cm⁻¹. ^d $V_3 = 83$ cm⁻¹; $V_6 = -7$ cm⁻¹; B = 5.15 cm⁻¹. ^e $V_3 = 405$ cm⁻¹; $V_6 = -15$ cm⁻¹; B = 5.0 cm⁻¹.

TABLE II: Energy Levels (cm^{-1}) of the Internal Rotation of the Methyl Group of *cis*-o-Cresol in the S₀, S₁, and Ionic States

	S ₀		\mathbf{S}_{1}^{a}		ion ^b	
species	obsd	calcd ^c	obsd	calcd ^d	obsd	calcde
0a1	0	0	0	0	0	0
1e	0	0	0	1.1		0
2e		144		42		186
3a ₁	280	280	76	76	336	336
4e	280	281		101		337
5e		402		145		430
6a1	491	491		202	471	471
7e [°]		516		266		510

^a The zero-point energy is 36 421 cm⁻¹. ^b The ionization potential is 66 849 cm⁻¹. ^c $V_3 = 600$ cm⁻¹; $V_6 = -30$ cm⁻¹; B = 5.2 cm⁻¹. ^d $V_3 = 90$ cm⁻¹; $V_6 = -5$ cm⁻¹; B = 5.1 cm⁻¹. ^e $V_3 = 540$ cm⁻¹; $V_6 = 135$ cm⁻¹; B = 4.8 cm⁻¹.



Figure 5. Comparison of the observed intensity distribution of the dispersed fluorescence spectra with the calculated Franck-Condon factor for the CH_3 internal rotational mode.

The calculated energy levels are listed in Tables I and II together with the best-fit parameters. Relative intensity distributions of the fluorescence excitation and the dispersed fluorescence spectra provide us with a useful check of the potential curves in the S_0 and S_1 states and also with a relation of the potentials with respect to the torsional angle. Figure 5 shows the comparison between the observed intensity distribution and the calculated Franck-Condon factor. A good agreement is seen between them. In the trans isomer, the change of 60° of the potential minimum (that is, the stable conformation of the methyl group) between the S_0 and S_1 states was necessary to reproduce the observed intensity distribution. Figure 6 shows the potential curves and the energy levels in the S_0 and S_1 states for the trans and cis isomers.

Figure 6 also shows the potential energy curve and energy levels of the ionic state. The potential energy curve for the ionic state was determined from the two-color photoionization threshold spectrum. In the two-color ionization a first laser pumps the S_0 state molecule to a particular vibrational level of the S_1 state and a second laser probes the ionization threshold. Figure 7a shows



Figure 6. Potential energy curves of the internal rotation of the CH_3 group for the trans and cis isomers of *o*-cresol in the S_0 , S_1 , and ionic states.



Figure 7. (a) Two-color ionization threshold spectrum of the *cis-o*-cresol showing the ionization from the $3a_1$ internal rotational level of the S_1 state. (b) Comparison with the calculated Franck-Condon factor using the potential in Figure 6.

the two-color ionization spectrum of the cis isomer showing the transitions from the $3a_1$ level of the S_1 state to the internal rotational levels of the ion that have " a_1 " symmetry. From these measurements the ionization potential was determined to be 66 849 cm⁻¹ for the cis isomer and 66 758 cm⁻¹ for the trans isomer. The height of the threshold associated with the internal rotational levels is proportional to the Franck–Condon factor of the transition between the S_1 and the ionic states. Figure 7b shows the comparison of the relative intensity and the calculated Franck–Condon factor using the potential curves of Figure 6.

As is seen in Figure 6, the potential barrier for the methyl rotation is quite high (355 and 600 cm⁻¹ for trans and cis, respectively) in the S₀ state and especially for the cis isomer. This can be easily understood by the steric hindrance. On the other hand, in the S₁ state the potential barrier suddenly drops to 83 and 90 cm⁻¹, respectively, for the trans and cis isomers. Moreover, in the trans isomer the most stable conformation changes by 60° by the electronic excitation, which is the same behavior as that found for the *o*-fluorotoluene molecule.⁸ For both cis and trans

TABLE III: Potential Barrier Height (cm⁻¹) of the Internal Rotation of the Methyl Group of Cis and Trans Isomers of o- and m-Cresol in the S₀, S₁, and Ionic States

	o-cresol		<i>m</i> -c	resol
	cis	trans	cis	trans
S ₀	600	355	26	11
\mathbf{S}_{1}	90	83ª	211	213
ion	540	405	328ª	276ª

^a Conformation change from S₀.

isomers, the most stable conformation of the CH₃ group is same between the S_0 neutral molecule and the ion.

Kudchadker et al.9 calculated the potential curve of the internal rotation of o-cresol in the ground state and obtained the barrier to be 727 cm⁻¹ in the cis isomer and 30 cm⁻¹ in the trans isomer, while the experimentally determined values are 600 and 355 cm^{-1} , respectively. Therefore, the calculation underestimates the potential barrier of the trans isomer too much and more accurate calculation is necessary. Though it is not clear why the potential barrier drops so dramatically in the S1 state, one of the possibility is an increased intramolecular hydrogen bonding between the O atom in the OH group and the H atom in the methyl group due to the change of the electron density from the S_0 state to the S_1 state. For example, in phenol the stability of the hydrogen bonding of H atom of the OH group with another proton-acceptor molecule increases greatly in the S₁ state compared with the S₀ state.¹⁰ This is explained by an increase of the positive charge of the H atom of the OH group, which causes an increase of the negative charge of the O atom. Therefore, the attractive force between the O atom of the OH group and the H atom of the methyl group will increase in the S_1 state. The potential barrier of the methyl group internal rotation increases again in the ionic state. In the ionic state the contribution of the double-bond character to the C-C bond connecting the methyl group and the benzene ring increases, and this results in the enhancement of the hyperconjugation and a great increase of the potential barrier.

(9) Kudchadker, S. A.; Wilhoit, R. C.; Zwolinski, B. J. J. Phys. Chem. 1978, 82, 245

(10) Abe, H.; Mikami, N.; Ito, M. J. Phys. Chem. 1982, 86, 1768.

In Table III, the barrier heights for the internal rotation in S_0 , S₁, and the ion are summarized for the cis and trans isomers of o-cresol and also for the cis and trans isomers of m-cresol. The most characteristic difference between o- and m-cresol is the opposite relation in the barrier height between the S_0 and S_1 states. In o-cresol, the barrier height in S_0 greatly decreases in S_1 , while in *m*-cresol, the small barrier height in S_0 dramatically increases in S_1 . This characteristic is common for all the ortho- and meta-substituted toluenes and phenols so far studied.^{6,8}

As seen from Table III, the barrier height in S_0 decreases in the order cis-o-cresol, trans-o-cresol, cis-m-cresol, and trans-mcresol. This is the decreasing order of the steric hindrance between the two substituents. Similarly, this is also the decreasing order of the barrier height in the ionic state. Therefore, the barrier heights in the S₀ state of the neutral molecule and the ion in its electronic ground state are more or less related to the steric hindrance. Abrupt decrease of the barrier height in the S_0 state in going from o-cresol to m-cresol suggests that a short-range steric effect around the CH₃ group is important in the S₀ state. On the other hand, for the ionic state, a long-range steric effect seems to be predominant as shown by a smooth decrease of the barrier height with decrease of the hindrance. The short- and long-range steric effects are probably associated with a short-range repulsive force due to the overlapping of the electron clouds and a long-range repulsive force arising from Coulombic interaction, respectively. The unit positive charge carried by the ion is distributed over all atoms in the molecule. The net positive charges at the individual atoms produce the repulsive force between the nonbonded atoms. Since this repulsive force is a Coulombic interaction and a long-range force, it decreases gradually with the distance between the nonbonded atoms. This Coulombic repulsive force acting between the hydrogen atoms of CH₃ and the hydrogen atom of OH is probably responsible for the barrier height in the ion. The barrier height in S1 has no apparent relation to the degree of the steric hindrance. As far as the height is concerned, the barrier height is similar between the cis and trans isomers for both o- and *m*-cresol. This fact and also the higher barrier height of *m*-cresol than that of o-cresol totally deny primary involvement of the steric effect in the S₁ state, indicating a dominant contribution of the electronic structure to the barrier height as described before.

Registry No. o-Cresol, 95-48-7; diethyl ether, 60-29-7; p-dioxane, 123-91-1.

Two-Photon Absorption Spectroscopy of Ion Beams: $CS_2^+ \tilde{C}^2 \Sigma_a^+$ State Characterization

D. D. Evard, T. Wyttenbach, and J. P. Maier*

Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland (Received: November 14, 1988)

Two-photon absorption spectroscopy with a mass-selected beam of CS_2^+ ions was used to study the predissociative $\tilde{C}^2\Sigma_g^+$ state of CS_2^+ . The first photon pumped the $\tilde{B}^2\Sigma_u^+ \leftarrow \tilde{X}^2\Pi_{g,3/2}$ transition, and the second photon was used to scan through the $\tilde{C}^2\Sigma_g^+ \leftarrow \tilde{B}^2\Sigma_u^+$ transition. A rotational analysis of several bands in this spectrum has been made, and $B_0' = 0.1112$ (2) cm⁻¹ was obtained. The $\tilde{C}^2\Sigma_g^+$ state is linear with a C-S bond length of 1.538 (2) Å in the v = 0 level. The vibrational level with two quanta of excitation in the bending mode dissociates three times faster than the state with one quantum of excitation in the symmetric stretch even though the internal energy is comparable.

Introduction

The structure and energy levels of gas-phase polyatomic cations have been characterized by use of a wide variety of techniques such as photoelectron spectroscopy,¹⁻⁵ emission spectroscopy,⁶⁻¹⁰ absorption spectroscopy,^{11,12} and mass spectrometric¹³⁻¹⁷ methods. Photoelectron spectroscopy is an ideal method for mapping out

(5) Wang, L. S.; Reutt, J. E.; Lee, Y. T.; Shirley, D. A. J. Electron Spectrosc. Relat. Phenom. 1988, 47, 167.
(6) Mrozowski, S. Phys. Rev. 1941, 60, 730; Ibid. 1942, 62, 270; Ibid.

⁽¹⁾ Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. Molecular Photoelectron Spectroscopy; Wiley-Interscience: London, 1970. (2) Potts, A. W.; Fattahallah, G. H. J. Phys. B. 1980, 13, 2545.

⁽³⁾ Kovac, B. J. Chem. Phys. 1983, 78, 1684.

⁽⁴⁾ Eland, J. H. D. Photoelectron Spectroscopy; Butterworths: London, 1984.

^{1947, 72, 682, 691.}