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Autoionization-detected infrared spectroscopy of intramolecular hydrogen bonds in aromatic cations. II. Unconventional intramolecular hydrogen bonds

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A newly developed infrared spectroscopic technique, called autoionization-detected infrared (ADIR) spectroscopy, was applied for a study on hydroxyl-alkyl interactions in cresol and ethylphenol cations. In this technique, vibrational transitions in the ion core of high Rydberg states, which has almost the same vibrational structure as the corresponding bare molecular ion, are measured by detecting the vibrational autoionization signal. The OH stretching vibrations in the rotational isomers of the *ortho*-, *meta*-, and *para*-cresol cations and those of the ethylphenol cations were observed. Remarkable low-frequency shifts of the OH vibration were found only for the *cis* rotational isomers of the *ortho*-cresol and *ortho*-ethylphenol cations, whereas no such shift was found for all the other rotational and structural isomer cations. On the other hand, no remarkable shift of the OH stretch frequency was found for all the isomers in the neutral ground state. These results indicate that an intramolecular hydrogen bond is formed between the hydroxyl and alkyl groups in the cationic ground state of *ortho*-cresol and *ortho*-ethylphenol. The remarkable low-frequency shift of the OH vibration also indicates that the alkyl group acts as a proton acceptor in the hydrogen bond. This is a new type of intramolecular hydrogen bond, and the origin of such unconventional hydrogen bond in the cations is discussed. © 2000 American Institute of Physics. [S0021-9606(00)00301-9]

I. INTRODUCTION

Hydrogen bonds involving alkyl groups have long been controversial subjects in chemistry.^{1,2} Alkyl groups are usually considered to exhibit no proton-donating or -accepting ability and not to participate in ordinary hydrogen bonds. Recently, however, several examples for extremely weak CH \cdots X hydrogen bonds have been reported in spectroscopic and theoretical studies,¹⁻¹² in which the alkyl group is regarded as a proton-donating site of the hydrogen bond, because of a larger electronegativity of carbon than that of hydrogen. On the other hand, much fewer examples are known for the C \cdots HX type hydrogen bonds.¹³⁻²² In a study on CH₄-H₂O complex, *ab initio* calculations predicted that the intermolecular binding energy (ΔE) of C \cdots HO is 0.78 kcal/mol, and is slightly more stable than the CH \cdots O bond ($\Delta E = 0.49$ kcal/mol).²¹ Actually, the former structure has been supported by a microwave spectroscopic study.¹³ Similar C \cdots HX (X=F, Cl, and CN) hydrogen bonds have been proposed for CH₄-HX¹⁵⁻¹⁸ and C₂H₆-HCN complexes.^{19,22}

Most of the studies on such hydroxyl-alkyl interactions so far concern those in their neutral ground state. Recent spectroscopic studies of hydrogen-bonded cluster cations have showed that the hydrogen bond strength drastically increases upon ionization.²³ This fact suggests that the hydrogen bond concerning alkyl groups in the cationic state would also be very different from that in the neutral state. In this

respect, alkyl-substituted phenol cations are expected to be an appropriate system for a spectroscopic study on such a weak hydroxyl-alkyl interaction. For alkyl-substituted phenols, there are many rotational and structural isomers corresponding to the different conformations and substitution positions of the hydroxyl group relative to the alkyl group. Such a difference in the conformation or the position leads to various strengths of the alkyl-hydroxyl interactions. Since the OH stretching vibration is known to be a quite sensitive probe of the hydrogen bond strength, a comparison of the OH stretch frequencies among the structural and rotational isomers both in the neutral and in its cation is expected to provide us with a direct information on the contribution of the alkyl group to hydrogen bond. The alkyl-hydroxyl interactions would be so weak that the spectroscopic investigation in condensed phases would not be adequate and the observation under an isolated condition eliminating any environment effects is required. Such a measurement can be performed by spectroscopic study in supersonic molecular beams.

Recent development of multiphoton and multicolor laser spectroscopic techniques enables us to apply infrared (IR) spectroscopy even to jet-cooled molecules.²⁴⁻³² For neutral jet-cooled species, the population labeling technique is often used to obtain IR absorption spectra of the sample with an extremely low concentration. This technique is called infrared-ultraviolet (IR-UV) double resonance spectroscopy, and studies on the inter- and intramolecular hydrogen bond structures have been carried out by observing the OH stretching vibrations.

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On the other hand, there had been no IR spectroscopic technique applicable to isolated cations of large polyatomic molecules in supersonic jets until we proposed a new technique in Part I of this series of papers.³³ The technique we proposed is based on the following concept: very high Rydberg states converging to the first ionization threshold are prepared by using two-color double resonance excitation. Their principle quantum numbers (n) are about 80–100, and the structure of their ion core can be regarded as almost the same as that of the corresponding bare molecular ion. Vibrational excitation of the ion core due to IR absorption induces vibrational autoionization, leading to the molecular ion. By monitoring the ion current due to the molecular ions, an IR spectrum is obtained as a function of the IR frequency. This technique is called autoionization-detected infrared (ADIR) spectroscopy.^{33–36} The concept of ADIR spectroscopy is essentially the same as that of photoinduced Rydberg ionization (PURI) spectroscopy,^{37–39} which has been used to observe electronic transitions of molecular cations. Very recently, Gerhards *et al.* proposed an IR spectroscopic technique similar to the above concept.⁴⁰

In a previous paper, we applied ADIR spectroscopic technique to the typical intramolecular hydrogen-bonded molecular cations, the fluorophenol and methoxyphenol cations.³³ We observed the OH stretching vibrations of these cations, and we found that the low-frequency shifts of the OH frequency due to the intramolecular hydrogen bond become almost double upon the ionization, reflecting a drastic enhancement of the hydrogen bond strength in the cationic state.

In this paper, we report OH stretching vibrations of the cresol (methylphenol) and ethylphenol cations. Despite of the expectation that the alkyl group is “inert” against the hydroxyl group, remarkable low-frequency shifts of the OH frequency have been found only in “*ortho-cis*” isomer cations in which the hydroxyl group faces to the alkyl group.³⁵ This is clear evidence for the presence of unconventional intramolecular hydrogen bonds between the hydroxyl and alkyl groups, in which the alkyl group acts as a proton acceptor.

II. EXPERIMENT

IR-UV double resonance spectroscopy was used to observe the OH stretching vibrations of jet-cooled cresols and ethylphenols in the neutral (S_0) ground state, and ADIR spectroscopy to their cationic (D_0) ground state. Both techniques are described elsewhere in detail,^{27,33,34,41} and only a brief description is given here.

A. IR-UV double resonance spectroscopy for the neutral ground state

A pulsed UV laser with the wavelength fixed at the origin band of the S_1-S_0 transition of the molecules is used to ionize them with the resonance enhanced multiphoton ionization (REMPI). The intensity of the REMPI signal represents a measure of the population of the vibrational ground state. Prior to the UV laser, an IR laser pulse is introduced, and its wavelength is scanned. When the IR wavelength is resonant on a vibrational transition of the molecule, the IR

absorption induces a reduction of the population of the ground state, and is detected as a decrease of the REMPI signal intensity.

B. ADIR spectroscopy for bare molecular cations in the electronic ground state

Jet-cooled sample molecules are excited to very high Rydberg states ($n=80-100$) converging to the vibrationless level ($v=0$) of the electronic ground state of their cation by using two-color double resonance excitation via the S_1-S_0 transition. The IR laser light excites the ion core of the Rydberg states to the vibrationally excited level ($v=1$). Because of the vibrational energy in the ion core, the Rydberg states with the vibrationally excited ion core lie above the first ionization threshold. Energy exchange between the ion core and the Rydberg electron results in the spontaneous ejection of the electron, i.e., vibrational autoionization. After an appropriate delay time from the IR laser pulse, a pulsed electric field is applied to the interaction region, and the ions produced by autoionization are extracted into a time-of-flight mass spectrometer.⁴² The IR spectrum is obtained by monitoring the produced ion intensity as a function of the IR laser frequency. Observed vibrational frequencies are regarded as being practically identical to those of the corresponding bare ion because of the extremely weak interaction between the ion core and the high Rydberg electron.

Details of the conditions of the lasers and vacuum equipment are described in Part I of this paper.³³ All samples were purchased from the Tokyo Kasei Co. and Aldrich, and were used without further purification. All samples except *para*-ethylphenol were kept at room temperature. In the case of *para*-ethylphenol, the sample was heated up to 350 K.

III. RESULTS AND DISCUSSION

A. Cresol

1. Structural and rotational isomers

Among three structural isomers of cresol, i.e., *ortho* (*o*-), *meta* (*m*-), and *para* (*p*-) isomers, there exist two rotational isomers, *cis* and *trans* for *o*- and *m*-isomers, as shown in Fig. 1. For the *m*- and *p*-isomers, alkyl–hydroxyl interactions are not expected because of a spatial separation between the two substituents. For the *o*-isomer, on the other hand, alkyl–hydroxyl interactions would be anticipated. It has been established for aromatic compounds that the vibrational spectra of rotamers of a particular structural isomer are quite similar to each other, but that their origins of the electronic transition are significantly different from each other.⁴³ In this respect, the utilization of electronic transitions enables us to distinguish these rotational isomers; this is a great advantage of the IR-UV double resonance and of the ADIR spectroscopic techniques.

Figure 2 shows the REMPI spectrum of the S_1-S_0 transition of jet-cooled *o*-cresol in the origin region. An intense band appears at $36\,421\text{ cm}^{-1}$, and a progression consisting of four bands is seen around $36\,200\text{ cm}^{-1}$. These two different type bands are assigned to the origin bands of the *cis* and *trans* isomers of *o*-cresol. The progression of the four bands is attributed to the internal rotation of the methyl group. Aota

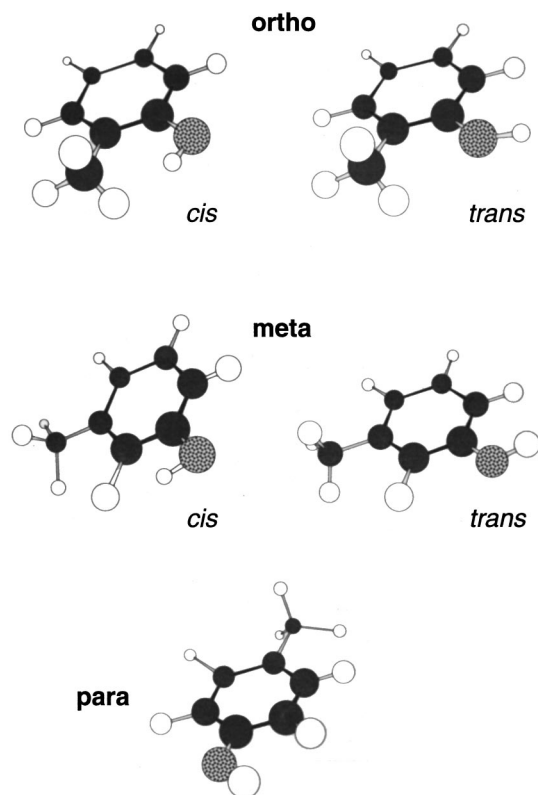


FIG. 1. Schematic representation of possible structural and rotational isomers of cresol.

et al. analyzed this progression, and showed that the potential minimum of the methyl conformation changes by 60° upon the S_1-S_0 transition.⁴⁴ On the other hand, the origin band of the other isomer shows a single intense peak at 36421 cm^{-1} and no progression due to the methyl rotation is found, indicating that the methyl conformation does not change upon the S_1-S_0 excitation. Aota *et al.* examined the cluster formation ability and assigned the single band at 36421 cm^{-1} to the *cis* isomer and the progression of the four bands to the *trans* isomer.⁴⁴ In the present study, we also carried out similar experiments to confirm their assignments.

With the addition of water vapor to the gaseous mixture for the jet expansion, a complicated vibronic structure originated at 35878 cm^{-1} appears in the electronic spectrum of *o*-cresol, as is shown in Fig. 3(a)(ii). This new structure is

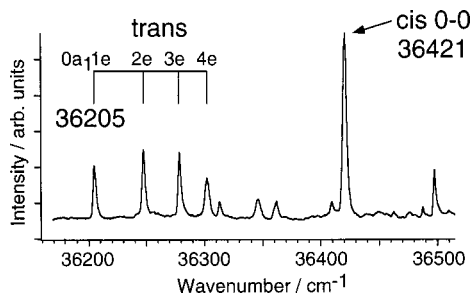
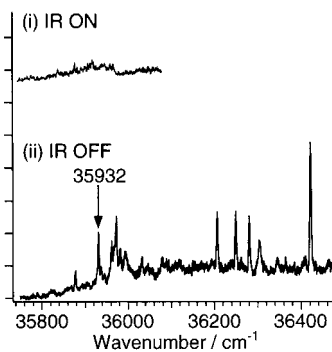


FIG. 2. Resonance enhanced multiphoton ionization (REMPI) spectrum of the S_1-S_0 transition of jet-cooled *o*-cresol in the origin region. Two band groups correspond to the *cis* and *trans* rotational isomers of *o*-cresol (see the text).

(a) Fluorescence excitation spectra



(b) IR-UV spectrum

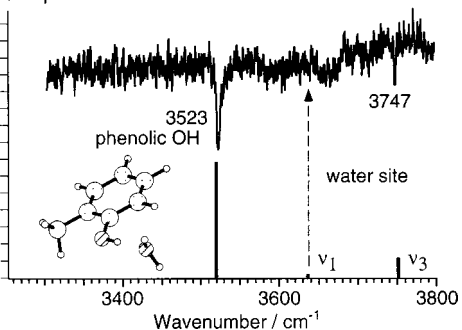


FIG. 3. (a) Fluorescence excitation spectra of the S_1-S_0 transition of the jet-cooled *o*-cresol- $(\text{H}_2\text{O})_1$ cluster (i) with the IR laser being fired before the UV laser and fixed at the OH stretching vibration in the neutral ground state (3523 cm^{-1}), (ii) without the IR laser (see the text). Two band groups above 36200 cm^{-1} are due to the rotational isomers of the *o*-cresol monomer. (b) IR-UV spectrum of the OH stretching vibrations of *o*-cresol- $(\text{H}_2\text{O})_1$ cluster in the neutral ground state. The UV laser wavelength is fixed at the band indicated by the arrow in the spectrum (a)(ii) (35932 cm^{-1}). The *ab initio* minimum energy structure of the cluster is shown in the inset. The calculated IR spectrum based on the *ab initio* structure is also displayed with the observed spectrum.

attributed to the S_1-S_0 electronic transition of the *o*-cresol-water cluster. When the UV laser wavelength is fixed at the 35932 cm^{-1} band in the new vibronic structure (indicated by the arrow in the figure) and the IR laser wavelength is scanned, the IR-UV double resonance spectrum is obtained as shown in Fig. 3(b). The IR spectrum showed the typical pattern of the OH stretching vibrations in the 1:1 hydrogen-bonded cluster of substituted phenol with water.⁴¹ The band at 3523 cm^{-1} is assigned to the phenolic OH of the *o*-cresol site which acts as a proton donor, and the band at 3747 cm^{-1} to the antisymmetric OH stretch of the water site as an acceptor.

The isomer separation of the cluster bands in the electronic spectrum can be performed by the IR-hole burning technique.⁴⁵ In this technique, the IR laser with wavelength fixed at the phenolic OH stretch band (3523 cm^{-1}) is introduced prior to the UV pulse, and the UV laser wavelength is scanned in the region of the cluster band by monitoring the fluorescence signal due to the electronic transition. All the vibronic bands attributed to the isomer probed by the IR laser disappear in the spectrum, while no change in intensity occurs for those of other isomers having different OH frequencies. Figure 3(a)(i) shows the results of the IR-hole burning spectroscopy. All the sharp vibronic bands in this

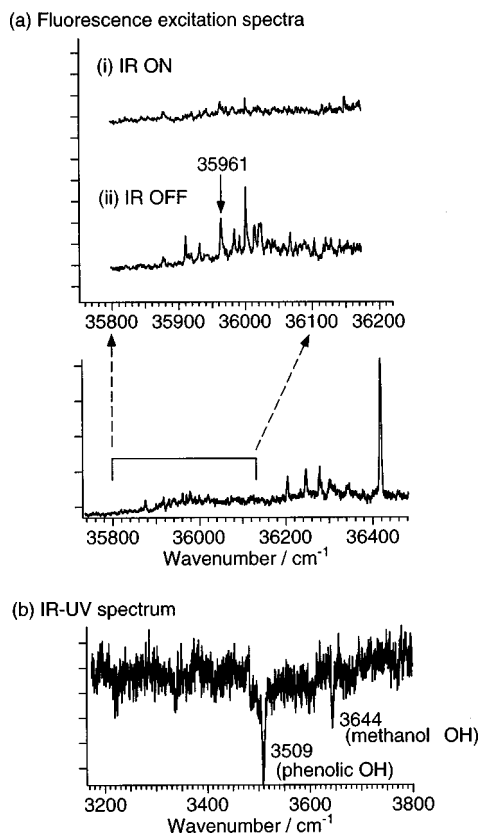


FIG. 4. (a) Fluorescence excitation spectra of the S_1 - S_0 transition of jet-cooled *o*-cresol-(methanol)₁ cluster (i) with the IR laser, (ii) without the IR laser. The IR frequency is fixed at 3509 cm^{-1} . (b) IR spectrum of the OH stretching vibrations of *o*-cresol-(methanol)₁ cluster in the neutral ground state. The UV laser is fixed at the band indicated by the arrow in the spectrum (a)(ii) (35 961 cm^{-1}).

region disappear with the IR laser hole burning, and it is concluded that only one isomer is present for the *o*-cresol-(H₂O)₁ cluster in the jet expansion.

Similar measurements were performed for the *o*-cresol-methanol and -dioxane clusters, as shown in Figs. 4 and 5, respectively. In both cases, complicated vibronic structures due to the cluster appear around 35 900 cm^{-1} , and the IR-UV spectra indicate the hydrogen-bonded cluster structures, in which *o*-cresol acts as a proton donor and methanol (or dioxane) is a proton acceptor. The IR-hole burning spectra show that only one isomer is present for each 1:1 cluster [in the case of *o*-cresol-dioxane, the broad background in the electronic spectrum shown in Fig. 5(a) is considered to be due to large-sized clusters, which are responsible for the broad absorption seen in the blue side of the sharp OH band in the IR spectrum shown in Fig. 5(b)].

When *o*-cresol acts as a proton donor in the 1:1 cluster, the cluster formation of the *cis* isomer is probably prevented by the steric hindrance of the methyl group while the *trans* isomer is free from the hindrance. In fact, *ab initio* calculations by the GAUSSIAN94 program package⁴⁶ with the Hartree-Fock (HF)/6-31G level predict that even with water, only the *trans* isomer forms a stable 1:1 cluster, and the *cis* isomer has no potential minimum for clusters. The calculated IR spectrum for the cluster of the *trans* isomer with water reproduces well the observed IR spectrum, as shown in

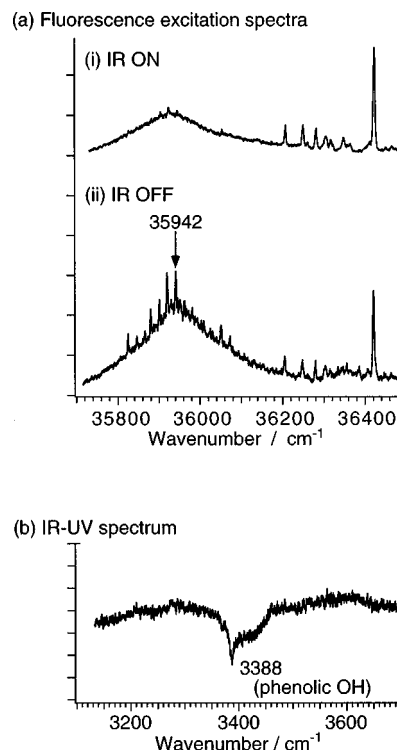


FIG. 5. (a) Fluorescence excitation spectra of the S_1 - S_0 transition of the jet-cooled *o*-cresol-(dioxane)₁ cluster (a)(i) with the IR laser, (ii) without the IR laser. The IR frequency is fixed at 3388 cm^{-1} . (b) IR spectrum of the OH stretching vibrations of *o*-cresol-(dioxane)₁ cluster in the neutral ground state. The UV laser is fixed at the band indicated by the arrow in the spectrum (a)(ii) (35 942 cm^{-1}).

Fig. 3(b). Therefore, it is reasonably concluded that all the observed clusters of *o*-cresol are attributed to those of the *trans* isomer. In all the electronic spectra of the clusters, intense and complicated low-frequency (10–50 cm^{-1}) progressions appear; such a spectral feature is in contrast with the spectra of 1:1 clusters of phenol with solvent,⁴¹ in which intense origin bands appear but intermolecular vibrations show short and weak progressions. The complicated spectra observed in the *o*-cresol clusters are interpreted as a result of the coupling between the internal rotation of the methyl group and the intermolecular vibrations. Therefore, it is indicated that the methyl conformation in the clusters changes upon the electronic excitation. Since the influence of the cluster formation on the internal rotation of the methyl group would not be significant, the cluster spectra strongly suggest that the displacement of the methyl conformation occurs also in the bare *trans* isomer. Therefore, the progression consisting of the four bands in the monomer spectrum is attributed to the *trans* isomer, and the single band at 36 421 cm^{-1} is assigned to the *cis* isomer. This conclusion is consistent with that in the early study by Aota *et al.*⁴⁴

The above assignments of the rotational isomer based on the cluster formation ability are also confirmed by *ab initio* calculations. Suzuki and Iwata calculated the potential energy surface of the methyl rotation in the S_0 , S_1 , and D_0 both for the *cis* and *trans* isomers of *o*-cresol.⁴⁷ They found that the calculated potential minimum of the *trans* isomer changes by 60° between S_0 and S_1 , while that of the *cis*

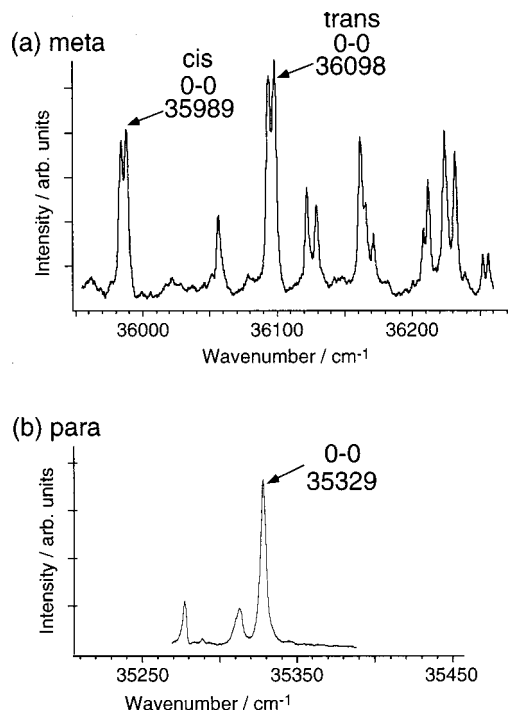


FIG. 6. REMPI spectra of the S_1-S_0 transition of jet-cooled (a) *m*- and (b) *p*-cresol in the origin region. (a) The two intense peaks at 35 989 and 36 098 cm^{-1} are assigned to the origin bands of the *cis* and *trans* isomers, respectively. (b) The intense peak at 35 329 cm^{-1} is the origin band.

isomer shows the minimum at the same conformation in S_0 and S_1 . The validity of these potential surfaces is verified by the fact that their calculations reproduce very well the methyl rotational band structure which is observed in the S_1-S_0 and D_0-S_1 electronic spectra.^{44,48}

Figures 6(a) and 6(b) show the REMPI spectra of the S_1-S_0 transitions of the jet-cooled *m*- and *p*-cresol, respectively. The fluorescence excitation spectrum of *m*-cresol was reported by Mizuno *et al.*,^{49,50} and the two intense peaks at 35 989 and 36 098 cm^{-1} were assigned to the origin bands of the *cis* and *trans* isomers, respectively. The splitting of the origin bands is due to the internal rotation of the methyl group. In the case of *p*-cresol, no rotational isomer is expected, and the intense peak at 35 329 cm^{-1} in Fig. 6(b) is the origin band. The observed REMPI spectrum reproduces well that reported by Tembreull *et al.*⁵¹

2. The OH stretching vibration in the neutral ground state

Figure 7 shows the IR-UV double resonance spectra in the OH stretching region of *o*-, *m*-, and *p*-cresol. In these spectra, the UV laser frequency was fixed at the origin band of the S_1-S_0 transition of each isomer, and the IR laser frequency was scanned while the REMPI signal intensity was monitored. OH frequencies of all the rotational and structural isomers are quite similar to each other (within 3 cm^{-1}), and are very close to that of phenol (3657 cm^{-1}). The similar OH frequencies for the *cis* and the *trans* rotational isomers of *o*-cresol clearly represent that the alkyl-hydroxyl interaction through space is negligible in the neutral ground state. This result is quite consistent with the extremely weak

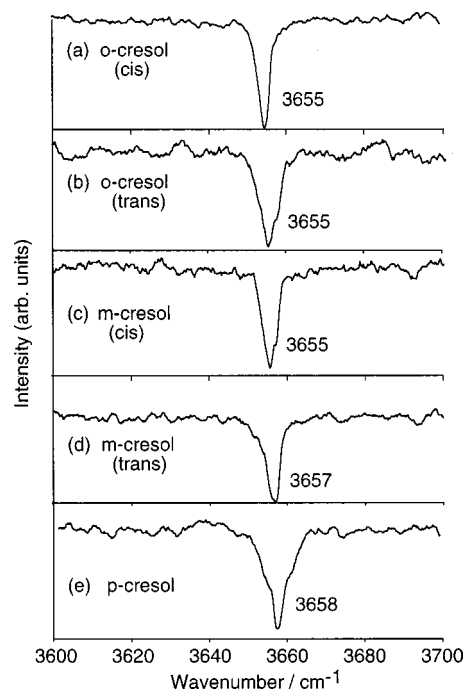


FIG. 7. Infrared spectra of the OH stretching vibrations of cresol in the neutral ground state measured by using the IR-UV double resonance technique. (a) *cis* and (b) *trans* rotational isomers of *o*-cresol, respectively. (c) *cis* and (d) *trans* isomers of *m*-cresol, respectively. (e) *p*-cresol.

hydrogen-accepting and -donating abilities of the methyl group, which is well-known for most cases. In *o*-fluorophenol and *o*-methoxyphenol, the low-frequency shifts relative to other isomers were found for their *cis* isomers. This is clearly due to intramolecular hydrogen bond formation, and the shifts are 25 and 49 cm^{-1} , respectively.^{33,52}

The very weak structural isomer dependence of the OH frequency in cresol indicates that the perturbation to the force field of the hydroxyl group caused by the methyl substitution is also very small. In the case of fluorophenol and methoxyphenol, the OH stretch frequency shifts from that of phenol by 2–7 cm^{-1} even in the *m*- and *p*-isomers.³³

3. The OH stretching vibration in the cationic ground state

ADIR spectra of the OH stretching vibrations in the rotational and structural isomers of the cresol cations are shown in Fig. 8. In these spectra, except for the *ortho-trans* isomer, the high Rydberg states converging to the vibrational ground state of the cation are pumped by two-color double resonance excitation via the zero-point level in S_1 , and the IR absorption of the ion core is observed by monitoring the autoionization signal intensity. In the case of the *ortho-trans* isomer, the Franck-Condon factor for the 0–0 band of the D_0-S_1 transition is so small that the double resonance pumping via the $3a_1$ level of S_1 is used to prepare the high Rydberg states in the vibrational ground state.

The observed OH frequencies of the cations are tabulated in Table I with those of the neutral cresol. The OH stretching frequencies of all the isomer cations were found to be substantially low-frequency-shifted over 100 cm^{-1} upon

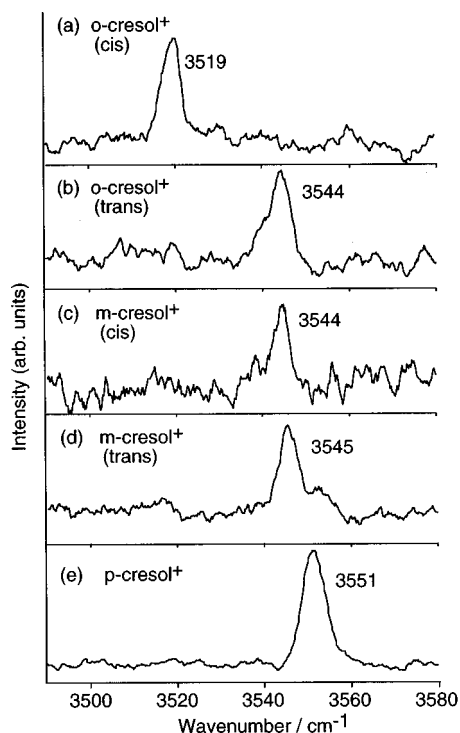


FIG. 8. ADIR spectra of the OH stretching vibrations of the cresol cations in the electronic ground state. (a) *cis* and (b) *trans* rotational isomers of the *o*-cresol cations, respectively. (c) *cis* and (d) *trans* isomers of the *m*-cresol cations, respectively. (e) *p*-isomer of the cresol cations.

the ionization. A similar shift was also observed for the phenol and other substituted phenol cations.^{33–35,40} This phenomenon is qualitatively explained by an enhancement of the double bond character of the C–O bond in the cation.^{53,54} Such an increase of the C–O bond order leads to a decrease of the electron density of the OH bond, resulting in the low-frequency shift of the OH frequency.

A significant feature of the observed ADIR spectra of the cresol cations is that only the *ortho-cis* isomer exhibits the much lower frequency shift for the OH stretch, while all the other rotational and structural isomers show the very similar OH frequencies. This result is rather unexpected, demonstrating that there is an interaction between the hydroxyl and methyl groups in the *ortho-cis* isomer cation. If the interaction occurs through the aromatic ring, the OH frequency shift is expected to be similar to that in the *trans* isomer of the *o*-cresol cation. However, the OH frequency difference between the *cis* and *trans* isomers is 25 cm⁻¹, and the latter exhibits OH frequency very similar to that of the other structural isomers. Therefore, the characteristic OH frequency shift only for the *ortho-cis* isomer indicates the inter-

action between the methyl and hydroxyl groups through space. Since the OH frequency shift due to interactions through space is characteristic of hydrogen bonding, we would call this interaction “intramolecular hydrogen bond.” The low-frequency shift of the OH frequency in the *cis* isomer means that the hydroxyl group is a proton donor and the methyl group acts as a proton acceptor in this intramolecular hydrogen bond. Such an intramolecular hydrogen bond has never been found, and this is the first observation of a new type of intramolecular hydrogen bond.

In contrast to the C---H–O type intramolecular hydrogen bond in the *ortho-cis* isomer of the cresol cation, no evidence is observed for the C–H---O type intramolecular hydrogen bond which is expected in the *trans* isomer. In the case of intermolecular hydrogen-bonded cluster cations, it has been reported that the proton-accepting OH group shows a low-frequency shift of a few tens of cm⁻¹.^{55–57} In this respect, a low-frequency shift of the OH stretch is also expected for the *trans* isomer if it forms a C–H---O type intramolecular hydrogen bond. The *trans* isomer, however, has almost the same OH frequency as the *m*- and *p*-isomers, indicating no contribution of the C–H---O type intramolecular hydrogen bond. The methyl rotational band analysis⁴⁴ and *ab initio* calculations⁴⁷ show that the C–H---O angle is 60° in the *trans* isomer of the *o*-cresol cation. This fact also supports the negligible effect of the C–H---O type intramolecular hydrogen bond.

The OH frequencies of the *m*- and *p*-isomer cations are similar to that of the phenol cation (3534 cm⁻¹),^{33,34} though a small blueshift from phenol is seen. This shift is clearly due to the electronic effect of the methyl substitution through the aromatic ring. Moreover, no frequency difference between the *cis* and *trans* isomers of the *m*-cresol cation is found, and this fact indicates that the intramolecular hydrogen bond between the methyl and hydroxyl groups is negligible in the *m*-isomer, as was observed in *S*₀. It is clear that the steric restriction prohibits the intramolecular hydrogen bond formation in the *m*-isomer. The similar behavior of *m*- and *p*-isomers was also found in the fluorophenol and methoxyphenol cations.³³

B. Ethylphenol

1. Structural and rotational isomers

Among three structural isomers of ethylphenol, there also exist several rotational isomers originating from the relative conformation between the hydroxyl and ethyl groups. In the case of the *o*-isomer, four energy minima corresponding to rotational isomers (I–IV) shown in Fig. 9 were found with *ab initio* calculations (GAUSSIAN 94: HF/6-31G),

TABLE I. OH stretching vibrational frequencies of cresol in cm⁻¹.

	<i>ortho</i> <i>cis</i>	<i>trans</i>	$\Delta\nu_{\text{OH}}^a$	<i>meta</i> <i>cis</i>	<i>trans</i>	<i>para</i>	phenol ^b
<i>S</i> ₀	3655	3655	0	3655	3657	3658	3657
<i>D</i> ₀	3519	3544	25	3544	3545	3551	3534

^a $\Delta\nu_{\text{OH}} = \nu_{\text{OH}}(\text{ortho-trans}) - \nu_{\text{OH}}(\text{ortho-cis})$.

^bFrom Refs. 33 and 34.

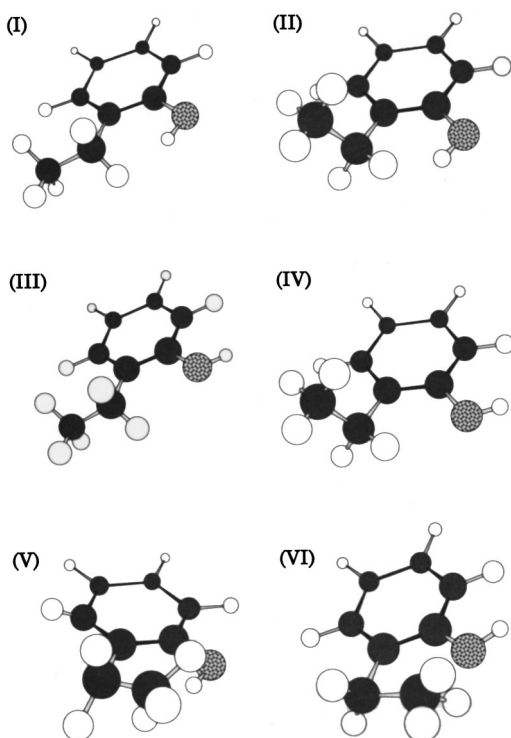


FIG. 9. Schematic representation of possible rotational isomers of *o*-ethylphenol.

and their relative total energies (zero-point energy corrections are included) are tabulated in Table II. Both isomer (I) and (II) have the *cis* conformation of the hydroxyl group relative to the ethyl group, and the ethyl group is perpendicular to the aromatic ring plane in isomer (II), while the ethyl group is in the aromatic ring plane in isomer (I). The *ab initio* calculations predict that the total energy of isomer (II) is more stable by 0.0474 eV than that of isomer (I). The *trans* conformation of the hydroxyl group also has two isomers (III and IV) according to the ethyl conformation, and isomer (IV) is more stable by 0.0479 eV than that of isomer (III). Though two other isomers (V) and (VI) shown in Fig. 9 may be considered for *o*-ethylphenol, no potential minima corresponding to these isomers were obtained in our calculations. In these structures, the steric repulsion between the hydroxyl and ethyl groups is so large that the corresponding local minima may not exist or may be too shallow to be found.

Shown in Fig. 10 are REMPI spectra of the origin region

TABLE II. Calculated energies of structural and rotational isomers of ethylphenol. The calculation level is HF/6-31G.

	Rotational isomer	Relative energy /eV
<i>ortho</i> -	isomer (I)	0.0996
	isomer (II)	0.0522
	isomer (III)	0.0479
	isomer (IV)	0.0000 (lowest)
<i>meta</i> -	isomer (II)	0.0533
	isomer (V)	0.0000 (lowest)

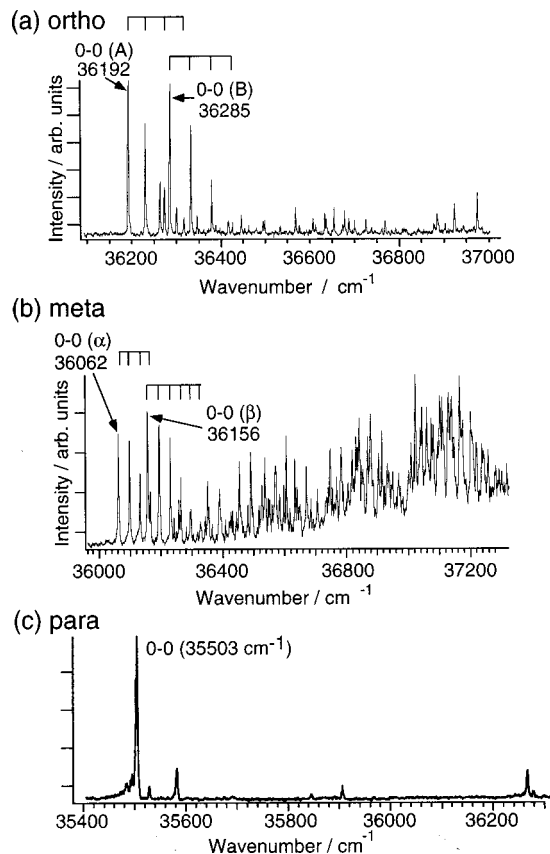


FIG. 10. REMPI spectra of the S_1-S_0 transitions of jet-cooled (a) *o*-, (b) *m*-, and (c) *p*-ethylphenol in the origin region, respectively. In spectrum (a), two bands A and B correspond to the origins of different rotational isomers of *o*-ethylphenol. (b) Two bands α and β correspond to the origins of different rotational isomers. (c) The most intense peak at $35\,510\text{ cm}^{-1}$ is the origin band.

of the S_1-S_0 transition of jet-cooled (a) *o*-, (b) *m*-, and (c) *p*-ethylphenol, respectively. In the case of the *o*-isomer, several bands having comparable intensities are seen in this region, and they are origin bands of rotational isomers of *o*-ethylphenol and their vibronic bands. The lowest frequency band at $36\,192\text{ cm}^{-1}$ is readily assigned to the origin band of a rotational isomer. To find origin bands of other rotational isomers, we measured two-color ionization thresholds via these bands. As seen in Fig. 11, two-color ionization via the $36\,285\text{ cm}^{-1}$ band shows a much lower threshold in the total energy than that via the $36\,192\text{ cm}^{-1}$ band; therefore, the band at $36\,285\text{ cm}^{-1}$ is assigned to the origin band of another rotational isomer. Hereafter, we refer to the spectral carriers associating with the bands at $36\,192$ and $36\,285\text{ cm}^{-1}$ as isomers A and B, respectively, and their structures are discussed in Sec. III B 3. Other bands in this region show the same ionization threshold as isomer A or B and they are assigned to the vibronic bands which originate from either the $36\,192$ or the $36\,285\text{ cm}^{-1}$ band, as shown in Fig. 10(a). Though four rotational isomers are predicted in the *ab initio* calculations of *o*-ethylphenol, only two of them were observed in the jet-cooled condition.

For the *meta* structural isomer, six rotational isomers corresponding to different conformation of the ethyl and hydroxyl groups are expected, as shown in Fig. 12. However,

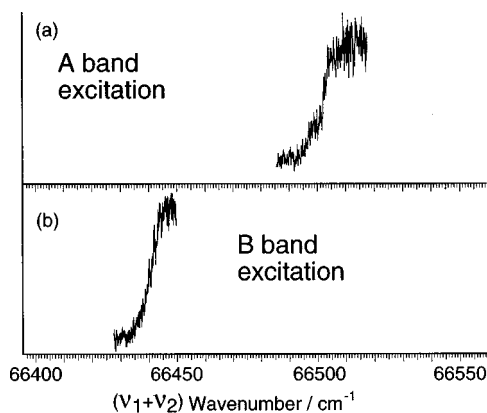


FIG. 11. Two-color, two-photon ionization spectra of *o*-ethylphenol around the first ionization threshold. The first excitation laser is fixed at the (a) *A* and (b) *B* bands of the S_1-S_0 transitions shown in Fig. 10(a), respectively. The second laser wavelength is scanned around the first ionization threshold.

ab initio calculations at the HF/6-31G level predict only two potential minima corresponding to isomers (II) and (V), in both of which the ethyl group is perpendicular to the plane of the phenyl ring. Both isomers are expected to have a very similar total energy as tabulated in Table II. In the REMPI spectrum of *m*-ethylphenol shown in Fig. 10(b), two bands at 36 062 and 36 156 cm^{-1} are assigned to the origin bands of these two rotational isomers. A long progression of low-frequency vibrations originates from each band, and very rich vibronic structures are observed in the higher vibrational energy region. Hereafter, we call the spectral carriers associating with the bands at 36 062 and 36 156 cm^{-1} isomers α and β , respectively. They correspond to the rotational iso-

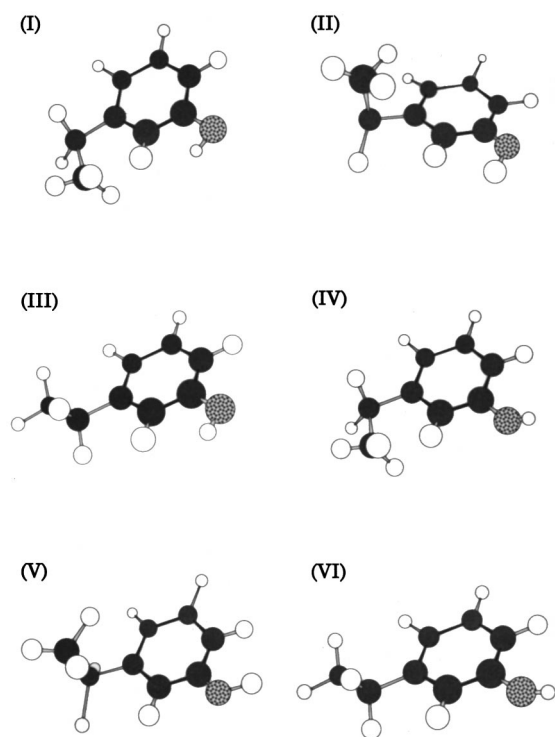


FIG. 12. Schematic representation of possible rotational isomers of *m*-ethylphenol.

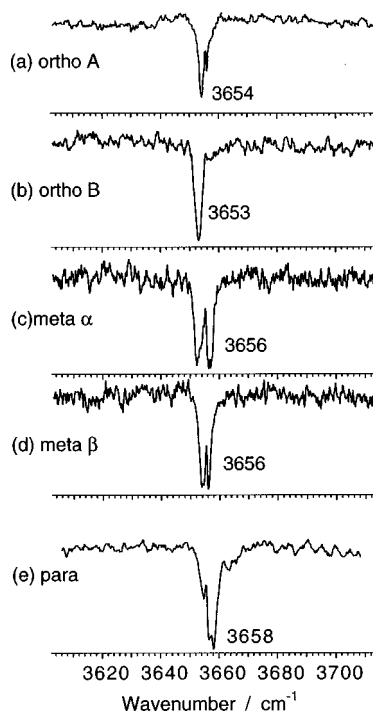


FIG. 13. Infrared spectra of the OH stretching vibrations of ethylphenol in the neutral ground state. (a) *A* and (b) *B* rotational isomers of *o*-ethylphenol, respectively. (c) α and (d) β rotational isomers of *m*-ethylphenol, respectively. (e) *p*-ethylphenol. The splitting of the bands is due to the IR absorption by atmospheric water in the optical path.

mers (II) and (V) predicted by the *ab initio* calculations, though it is difficult to determine which structure corresponds to which band in the electronic spectrum.

For *p*-ethylphenol, the most intense band at 35 503 cm^{-1} is assigned to the origin band, as shown in Fig. 10(c). It has been reported that only one isomer of *p*-ethylphenol exists in the jet expansion.^{36,58,59} The rotational analysis of the electronic transition determined the molecular structure in which the ethyl group is perpendicular to the aromatic ring plane.⁵⁹ We also performed *ab initio* calculations at the HF/6-31G level, and confirmed that this nonplanar structure is the global potential minimum.³⁶

2. The OH stretching vibration in the neutral ground state

Figure 13 shows IR-UV double resonance spectra in the OH stretching vibrational region of the isomers of *o*-, *m*-, and *p*-ethylphenol. No clear rotational isomer dependence of the OH stretch frequency is found, whereas slight shifts (within 5 cm^{-1}) are seen between the structural isomers. Moreover, these OH stretch frequencies are very close to that of free phenol (3657 cm^{-1}), indicating that the ethyl substitution causes a negligible perturbation on the force field of the OH stretching mode, as was also found for the methyl substitution. It should be noted that the splitting of bands is due to the infrared light absorption of the atmospheric water in the optical path. As in the case of cresol, no sign of the intramolecular hydrogen bond between the hydroxyl and ethyl group is found even for the *o*-isomer, and the ethyl group is quite inert to the hydroxyl group.

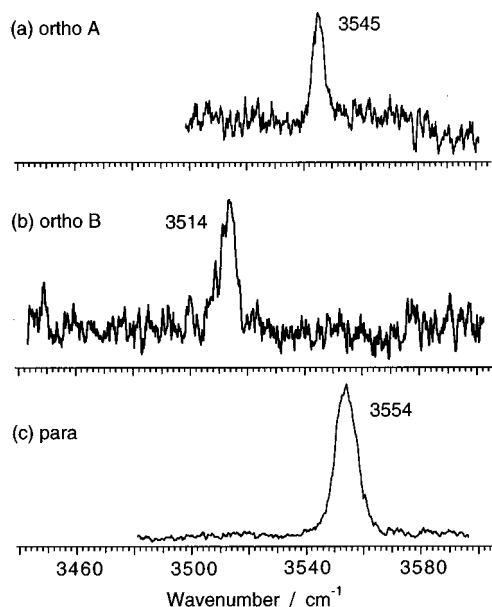


FIG. 14. ADIR spectra of the OH stretching vibrations of the ethylphenol cations in the electronic ground state. (a) *A* and (b) *B* rotational isomers of the ethylphenol cations. (c) *p*-ethylphenol cation.

3. The OH stretching vibration in the cationic ground state

ADIR spectra of the OH stretching vibrations of the *o*- and *p*-ethylphenol cations are shown in Fig. 14 and the OH frequencies are tabulated in Table III. As for the *m*-isomer cations, we could not observe the ADIR spectrum because the poor Franck–Condon factors from the S_1 state make a sufficient generation of high Rydberg states difficult. The OH stretching frequencies of the *o*- and *p*-isomers cations were substantially reduced over 100 cm^{-1} upon the ionization, as was seen in the cresol cations. Though the two rotational isomers (*A* and *B*) of *o*-ethylphenol both exhibit very similar OH frequencies in the neutral ground state, they show a significant difference in the cationic ground state. While the OH frequency of the isomer *A* cation (3545 cm^{-1}) is similar to those of the phenol cation (3534 cm^{-1})^{33,34} and *p*-ethylphenol cation (3554 cm^{-1}), the isomer *B* cation shows much lower OH frequency (3514 cm^{-1}). This is a quite similar phenomenon to that found in the *o*-cresol cation, and the OH frequency difference between the isomer *A* and *B* cations (31 cm^{-1}) is also similar to that observed for the *o*-cresol cations. Therefore, it is reasonable to conclude that the drastic redshift of the isomer *B* cation is caused by the intramolecular hydrogen bond formation with the neighboring ethyl group, which acts as a proton acceptor.

To form the intramolecular hydrogen bond, the conformation of the isomer *B* cation should be such that the OH group faces to the ethyl group. Since the REMPI spectrum shows the strong 0–0 band of the S_1 – S_0 transition and the clear threshold appears in the two-color ionization, as shown in Figs. 10 and 11, respectively, it is also suggested that the conformation of isomer *B* in the S_0 state would be unchanged upon the ionization. Therefore, the conformation of the isomer *B* cation can be found among the *ab initio* structures for the S_0 state shown in Fig. 9. Isomers (I) and (II) include the *cis* conformation of the hydroxyl group, in which the hydroxyl group faces to the ethyl group, and isomer (II) is 0.0474 eV more stable in the total energy than isomer (I). Though much higher-level calculations would be required for an unequivocal determination of the conformation, the isomer (II) structure in Fig. 9 is the most probable for the isomer *B* of *o*-ethylphenol, which has the intramolecular hydrogen bond in the cationic ground state. The preference of the perpendicular conformation of the ethyl group over the in-plane conformation agrees with the results obtained for ethylbenzene^{60,61} and *p*-ethylphenol.^{36,58,59}

The isomer *A* of the *o*-ethylphenol cation, in which no evidence for the intramolecular hydrogen bond was found, might have the *trans* conformation of the hydroxyl group. As was shown in Fig. 9 and Table II, two rotational isomers having the *trans* conformation are predicted by the *ab initio* calculations. Isomer (IV) is the minimum energy conformer of the *o*-ethylphenol, and we tentatively assign isomer *A* to isomer (IV).

The OH stretch frequency of the *p*-isomer cation shows a slight high-frequency shift from that of the phenol cation. In the case of the *p*-isomer, the ethyl–hydroxyl distance is so long that this shift is clearly due to the electronic effect of the ethyl substitution through the aromatic ring. Such high-frequency shift was also found for the *p*-cresol cation, suggesting the similar electronic character of the methyl and ethyl groups.

C. Unconventional intramolecular hydrogen bond: Hydroxyl–alkyl interactions

In both *o*-cresol and *o*-ethylphenol, their *cis* isomer cations show the remarkable low-frequency shifts of the OH stretching vibration relative to that of the *trans*, while the *cis* and *trans* neutral isomers show essentially the same frequency. Because the electronic interactions between the hydroxyl and alkyl groups through the aromatic ring should be identical in the *cis* and *trans* isomers, the characteristic low-frequency shifts seen only in the *cis* isomers are clearly attributed to the interactions through space between these two

TABLE III. OH stretching vibrational frequencies of ethylphenol in cm^{-1} .

	<i>ortho</i>			<i>meta</i>		<i>para</i>	phenol
	isomer <i>A</i>	isomer <i>B</i>	$\Delta\nu_{\text{OH}}^a$	isomer α	isomer β		
S_0	3654	3653	1	3656	3656	3658	3657
D_0	3545	3514	31	3554	3534

^a $\Delta\nu_{\text{OH}} = \nu_{\text{OH}}(\text{ortho, isomer A}) - \nu_{\text{OH}}(\text{ortho, isomer B})$.

groups, i.e., intramolecular hydrogen bond. In this hydrogen bond, surprisingly, the alkyl group acts as a proton acceptor. This nature shows that it is a new type of intramolecular hydrogen bond. The OH frequency shift due to the intramolecular hydrogen bond of the *cis* isomer is 25 cm^{-1} in the *o*-cresol cation and 31 cm^{-1} in the *o*-ethylphenol cation. These shifts are as large as the shift due to the conventional intramolecular hydrogen bond (F---H-O) in neutral *o*-fluorophenol (25 cm^{-1}),^{33,52} suggesting the similar hydrogen bond strength.

The alkyl group has no lone pair electrons, and it is classified to be an electron-donating group to the aromatic ring through the interaction, so-called hyper conjugation. Thus, the interaction makes the hydrogen sites of the methyl group positively charged, and its positive nature is considered to increase upon ionization. Because of these reasons, it has been generally recognized that the alkyl group hardly acts as a proton acceptor. In fact, there have been very few reports on the C---H-O type hydrogen bond. The very weak C---H-O type intermolecular hydrogen bond has recently been predicted in *ab initio* calculations of the $\text{CH}_4\text{-H}_2\text{O}$ cluster.^{20,21} The bonding energy was estimated to be extremely small (0.78 kcal/mol), and it is hardly distinguished from a van der Waals bond. The *ab initio* calculations also predicted no OH frequency shifts due to the C---H-O bond formation,²¹ and it is consistent with the undetectable low-frequency shift of neutral *o*-cresol and *o*-ethylphenol. In this respect, it is strongly suggested that the C---H-O type hydrogen bond can be observed only in the cationic state, in which the hydrogen bond strength is significantly enhanced in general.

To elucidate the nature of the new type of intramolecular hydrogen bond, we attempted density functional calculations of the *cis* and *trans* isomers of *o*-cresol both in the neutral and cationic ground states. We used the GAUSSIAN 94 program package with the B3LYP functionals and 6-31G(*d,p*) basis set expansion.⁶² This calculation level has been successfully used to predict structures and vibrations of several aromatic cluster cations.⁶³ The OH stretching frequencies and key structural parameters based on the optimized structures are shown in Fig. 15.

The methyl conformation relative to the hydroxyl group is predicted to be unchanged between S_0 and D_0 , and this result is consistent with the previous studies on the methyl rotation in cresol.^{44,47,48} The calculations reproduce well the large low-frequency shift of the OH frequency upon the ionization for both isomers. The lengthening of the OH bond and shortening of the CO bond are also seen upon the ionization, indicating an enhancement of the double-bond character of the CO bond, which leads to weakening the OH bond, as was suggested in Sec. III A 3.

A sign of the intramolecular hydrogen bond should appear as differences of the OH frequencies and structural parameters between the *cis* and *trans* isomers. The calculations predict the lower OH stretching frequency and longer OH bond length for the *cis* isomer cation than the *trans* isomer cation. However, the calculated difference of the OH frequency (5 cm^{-1}) is much smaller than the observed one (25 cm^{-1}), and the difference in the bond length is also ex-

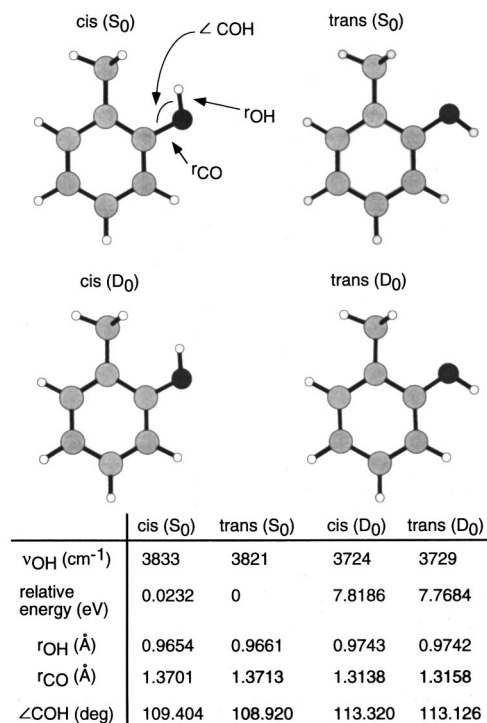


FIG. 15. The calculated structures of the *cis* and *trans* isomers of *o*-cresol in the neutral and cationic ground states. The calculation level is B3LYP/6-31G(*d,p*). The calculated OH frequencies and key structural parameters are shown in the figure. The relative energies include the zero-point energy corrections.

remely small. Moreover, the same level calculations for neutral *o*-cresol result in the difference of the OH frequency by 12 cm^{-1} between the *cis* and *trans* isomers. The IR-UV measurement demonstrated that both the isomers show the same OH frequency in the neutral ground state, and the intramolecular hydrogen bond is negligible. Therefore, the differences in the calculated frequencies and structures between the neutral *cis* and *trans* isomers represent the range of the error in this calculation level. The differences between the *cis* and *trans* isomer cations are as small as those between the neutrals, and it is concluded that the B3LYP/6-31G(*d,p*) level calculation is not high enough to treat so very delicate a hydrogen bond. Though the difference (by 25 cm^{-1}) in frequency is large enough to detect in spectroscopic experiments, it is quite tough work to discuss such a small value in theoretical calculations. Quantum chemical calculations of much higher levels are required to elucidate the nature of this intramolecular hydrogen bond.

An interesting explanation of the atypical intramolecular hydrogen bond may qualitatively be made in terms of the fact that the carbon atom can be a pentacoordinate site in cations.⁶⁴⁻⁶⁶ Quantum chemical 3-center 2-electron bond formation is considered to be essential in such nonclassical cations. The nature of pentacoordinated carbocations, such as CH_5^+ , has been theoretically and experimentally investigated.⁶⁴⁻⁶⁶ The increase of the positive charge distribution of the alkyl group upon the ionization might induce mixing of such nonclassical character which contributes to the intramolecular hydrogen bond. This also explains why the unconventional hydrogen bond occurs only in the cat-

ions. It is expected that observation of the CH stretching vibrations of the methyl group would give us direct information on the contribution of the pentacoordinated carbon character. Though we tried to observe the CH stretching vibration of the *o*-cresol cations by ADIR spectroscopy, we could not detect any autoionization signal in the CH stretch region. The B3LYP/6-31G(*d,p*) calculations predicted that the IR absorption intensities of the methyl CH stretches are only 0.1%–5% of that of the OH stretch both in the *cis* and *trans* *o*-cresol cations. The methyl CH stretch bands might be too weak to be observed by using the present ADIR technique. In conclusion, at the present stage it is quite difficult to give an unequivocal explanation for the origin of the unconventional hydrogen bond.

Finally, we would like to emphasize the following point: though enormous data on hydrogen bond have been accumulated for over 50 years, the topic of hydrogen bond is still a rapidly growing field. New concepts of hydrogen bond, such as X–H····· π ^{67,68} and X–H·····H–Y (Ref. 69) type hydrogen bonds, have been established in the last decade. Much of our present knowledge on hydrogen bonds is concerned with neutral molecules, while studies in cations are still scarce because of experimental and theoretical difficulties. Development of the ADIR spectroscopic technique enables us to find a new type of intramolecular hydrogen bond in the alkylphenol cations for the first time, because both the rotational isomer separation and complete elimination of solvation effects are required for the observation and characterization of this unconventional hydrogen bond between the hydroxyl and alkyl groups.

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