NH Stretching Vibrations of Jet-Cooled Aniline and Its Derivatives in the Neutral and Cationic Ground States

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Received: November 27, 2002; In Final Form: February 21, 2003

NH stretching vibrations of jet-cooled aniline and its various derivatives were observed in the neutral and cationic ground states. Infrared−ultraviolet double-resonance spectroscopy was utilized for the observation in the neutral ground state, and autoionization-detected infrared spectroscopy was used in the measurement of the cationic ground state. Low-frequency shifts of the NH frequencies were seen upon ionization, though the magnitude of the shifts was much smaller than those of the OH stretching vibrations observed for phenol derivatives. NH vibrational frequencies of meta and para isomers of aniline derivatives showed a positive correlation with the Hammett σ parameters of the substituents in the neutral ground state, while a negative correlation was found for the cationic ground state. Intramolecular hydrogen bond formation was found for *o*-cyanoaniline in both the neutral and cationic ground states based on the infrared spectra of deuterated isotopomers as well as theoretical calculations, showing that the hydrogen bond strength is remarkably enhanced upon ionization.

I. Introduction

In a series of our recent papers, we have reported a development of a new technique called autoionization-detected infrared (ADIR) spectroscopy, which enables us to carry out infrared (IR) spectroscopy of isolated bare molecular cations in molecular beams.[1−9] We applied this technique to various phenol derivative cations and determined OH stretching vibrational frequencies of these cations. In the case of phenol, the OH frequency showed a low-frequency shift of 123 cm^{-1} upon ionization, which is interpreted in terms of the mixing of the quinoid character.[1−4] As for ortho (o)-substituted phenols, it was found that intramolecular hydrogen bond strength between the hydroxyl and neighboring proton accepting groups is remarkably enhanced upon ionization.[2−4,6] The *o*-cresol (*o*-methylphenol) cation is the most remarkable example, exhibiting an unconventional intramolecular hydrogen bond in which the methyl group plays a role of the proton acceptor, while such an intramolecular hydrogen bond has never been found in its neutral state, as is well-known.[3,6] For meta (m)- and para (p)-substituted phenols, on the other hand, it was found that their OH frequency shifts in their cationic ground state strongly depend on the substituents, while all of their neutrals do not exhibit such a clear dependence.[7] Since the m- and p-substituents have no possibility of forming intramolecular hydrogen bonds even in the cationic state, it has been suggested that there must be characteristic electronic interactions between the hydroxyl group and substituted functions through the covalent bonds in the cationic aromatic ring.

Despite such a recent development in the study of OH stretching vibrations in aromatic cations by using the newly developed IR techniques, NH stretching vibrations in bare aromatic cations have scarcely been observed.[10] It is well-known that the amino group in aniline has a nonplanar structure in the neutral ground state (S_0), but it turns out to be quasi-planar in the cationic ground state (D_0).[11−14] The determination of the precise NH stretching vibrational frequencies in the aniline cation would greatly contribute toward understanding this characteristic behavior of the amino group upon ionization, though it has not yet been done.

Recently, NH stretching vibrations in hydrogen-bonded cluster cations involving aniline have extensively been studied to elucidate microsolvation structures concerned with the amino group.[15−26] These cluster studies have reported enhancement of the hydrogen bond strength upon ionization of the aniline moiety. This enhancement is similar to that of the hydrogen-bonded phenol cluster cation, indicating similar behavior in acidity of the proton donor site (the amino and hydroxyl groups).[27−30] On the other hand, no example has been reported for intramolecular hydrogen bond in aniline derivative cations. To interpret IR spectra of the cluster cations and also to study intramolecular hydrogen bonds in cations, information on the NH stretching vibrations in bare molecular cations has been strongly required.

Vibrational frequencies of cations have often been obtained by conventional time-of-flight and zero-kinetic energy (ZEKE) photoelectron spectroscopy,[13,31−34] but the NH stretching vibrations have never been observed because of their very low intensity in electronic transitions and of band congestion at the high vibrational energy region. Nakanaga et al. applied IR spectroscopy to the aniline cation by using the “messenger” technique.[15] In this technique, the aniline−Ar cluster cation was prepared by resonance-enhanced multiphoton ionization (REMPI) of the corresponding neutral cluster, and the IR absorption due to the NH stretching vibrations was detected by monitoring vibrational predissociation of the cluster cation. They observed the NH stretch bands at 3395 and 3488 cm^{-1} in the aniline−Ar cluster cation. Because the NH stretching bands of bare neutral aniline are seen at 3422 and 3508 cm^{-1}, the low-frequency shifts of the NH vibration upon the ionization are estimated to be −27 and −20 cm^{-1}, respectively.[15] The validity of such a messenger technique, however, is quite dependent on the magnitude of perturbations due to the Ar atom attachment, which may not be negligibly small.[5,25,35−37] In fact, Solcà and

10.1021/jp022504k CCC: $25.00 © 2003 American Chemical Society
Published on Web 04/19/2003

Dopfer produced aniline−Ar cluster cations by using a pick-up type ion source and demonstrated the presence of a more stable isomer cluster cation which exhibits much larger low-frequency shifts of the NH vibrations.[25] In this respect, unambiguous observation of the vibrational frequencies of the *bare* aniline cation without any perturbations due to solvation is highly desired to provide a definitive conclusion on the NH frequency shifts upon ionization.

Gerhards and co-workers observed the NH stretching vibration in the indole cations in a molecular beam by using their original IR technique called IR/PIRI.[10,20,38] They found a low-frequency shift of the NH vibration by 71 cm^{-1} upon ionization.[10] This is the unique example so far for the NH stretching vibration in isolated aromatic cations.

In the present paper, as a series of applications of ADIR spectroscopy, we report the investigation of NH stretching vibrations in the cationic ground state (D_0) of jet-cooled aniline and its various derivatives. The NH frequencies of the jet-cooled neutral species are also measured by using infrared−ultraviolet (IR−UV) double-resonance spectroscopy for comparison. Substituent effects on the NH stretching vibrations in m- and p-substituted anilines (methylaniline, fluoroaniline, cyanoaniline, and methoxyaniline) are discussed. In the o-substituted aniline cations (methylaniline, fluoroaniline, and cyanoaniline cations), intramolecular hydrogen bond formation between the amino group and the neighboring substituent is probed by the observation of the NH frequency. Details of the intramolecular hydrogen bond of *o*-cyanoaniline are also studied on its deuterated isotopomers. Density functional theory (DFT) calculations are carried out to confirm the observed intramolecular hydrogen bonds in o-substituted anilines.

II. Experiment

The NH stretching vibrations of jet-cooled aniline and its derivatives in the neutral ground state (S_0) are observed by IR−UV spectroscopy.[39−41] The ADIR spectroscopy is employed for the observation of the NH stretching vibrations in D_0. All of these techniques are described elsewhere in detail.[1,4,40] Only a brief description is given herein.

A. IR−UV Double-Resonance Spectroscopy for S_0. An UV laser pulse of which wavelength is fixed at the origin band of the S_1−S_0 transition of the molecule is introduced, and the REMPI signal is monitored as a measure of the population in S_0. An IR laser pulse is introduced prior to the UV laser pulse, and its wavelength is scanned. When the IR laser frequency is resonant with the NH stretching vibration(s) of the molecule in S_0, the reduction of the vibrational ground-state population occurs, and the depletion of the REMPI signal intensity is observed.

B. ADIR Spectroscopy for Molecular Cations in D_0. ADIR spectroscopy is an application of the concept of photoinduced Rydberg ionization (PIRI) spectroscopy, which has been used to observe electronic transitions of molecular cations.[42,43] Very high Rydberg states ($n = 80−100$) of the molecule converging on the adiabatic ionization energy level ($v = 0$) are prepared by two-color double-resonance excitation via the S_1−S_0 transition. The structure of the ion core of the Rydberg molecule can be regarded as the same as that of the bare molecular ion. An IR laser pulse is introduced with a few nanoseconds delay after the excitation of the Rydberg states, and its wavelength is scanned. When the IR laser excites the vibration of the ion core, the total (= electronic and vibrational) energy of the Rydberg states exceeds the first ionization threshold, and vibrational autoionization occurs. By monitoring the ion current generated by the autoionization, an IR spectrum of the ion core, which can be regarded as a spectrum of the bare cation, is observed. A pulsed electronic field is used to extract the ions into a time-of-flight mass spectrometer.

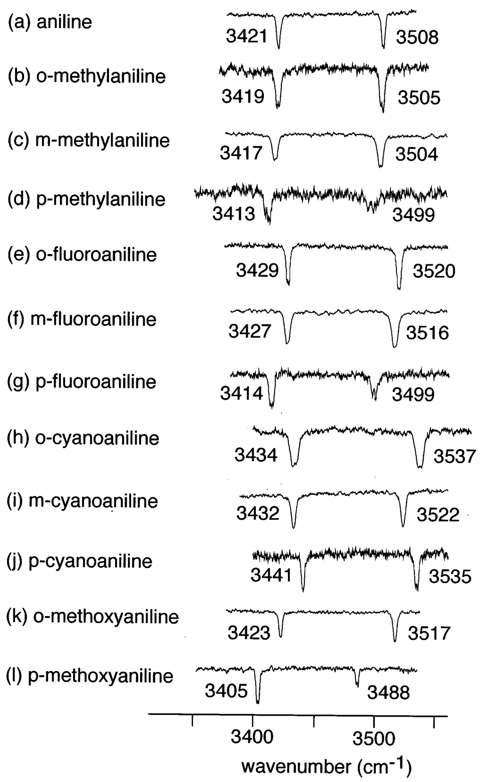

Figure 1. NH stretching vibrational region of IR spectra of (a) aniline and (b−l) monosubstituted anilines in the neutral ground state (S_0). The IR−UV double-resonance technique is used to measure the spectra.

The samples were heated to 340−400 K to obtain enough vapor pressure, and their vapor was seeded in He or Ar of 4 atm stagnation pressure. The gaseous mixture is expanded into a vacuum chamber through a pulsed valve. A typical background pressure of the chamber was 6×10^{-6} and 8×10^{-7} Torr with and without the valve operation, respectively. The jet expansion was skimmed by a skimmer of 2 mm diameter, and the resultant molecular beam was introduced into the interaction region. A time-of-flight mass spectrometer was used for the mass separation of ions.

In the measurement of deuterated isotopomers, a sample deuterated in its amino group was prepared by vacuum distillation of the sample dissolved in deuterated water.

III. Results

A. S_1−S_0 Electronic Spectra. Both of the IR−UV and ADIR spectroscopic techniques utilize the S_1−S_0 electronic transition to measure IR spectra in the S_0 and D_0 states, respectively. The electronic spectra of jet-cooled aniline and its derivatives have been extensively studied.[44−50] The S_1−S_0 origin band positions have been determined as follows: aniline, 34 029 cm^{-1}; *o*-methylaniline, 34 316 cm^{-1}; *m*-methylaniline, 33 813 cm^{-1}; *p*-methylaniline, 33 086 cm^{-1}; *o*-fluoroaniline, 34 583 cm^{-1}; *m*-fluoroaniline, 34 614 cm^{-1}; *p*-fluoroaniline, 32 652 cm^{-1}; *o*-cyanoaniline, 31 270 cm^{-1}; *m*-cyanoaniline, 31 716 cm^{-1}; *p*-cyanoaniline, 33 481 cm^{-1}; *o*-methoxyaniline, 33 874 cm^{-1}; and *p*-methoxyaniline, 31 581 cm^{-1}.

B. IR Spectra in S_0. Figure 1 shows IR spectra in S_0 of the NH stretching vibrational region for (a) aniline, (b) *o*-methylaniline, (c) *m*-methylaniline, (d) *p*-methylaniline, (e) *o*-fluoroaniline, (f) *m*-fluoroaniline, (g) *p*-fluoroaniline, (h) *o*-cyanoaniline, (i) *m*-cyanoaniline, (j) *p*-cyanoaniline, (k) *o*-methoxyaniline, and (l) *p*-methoxyaniline. The IR−UV double-resonance spectroscopic technique is utilized to measure the spectra, and the UV laser wavelength is fixed at the S_1-S_0 origin band of the sample. Two NH stretching vibrations of the amino group are readily identified in all the IR spectra, in which the lower frequency band is attributed to the symmetric NH stretch (ν_s) and the higher is to the antisymmetric NH stretch (ν_a). For example, the ν_s and ν_a bands of aniline in S_0 occur at 3421 and 3508 cm^{-1}, respectively. The NH frequencies of jet-cooled aniline have been reported by Nakanaga et al.,[15] and the present results agree well with them. An IR spectrum of *p*-cyanoaniline in a jet has also been observed by Sakota et al.[21] and is reproduced well in our measurement.

The ν_s and ν_a bands of aniline derivatives exhibit low- or high-frequency shifts with respect to those of aniline, depending on the substituent; the NH stretches in all of methylanilines and methoxyanilines are low-frequency-shifted, while those in all cyanoanilines are shifted to the high-frequency side. As for fluoroanilines, the o- and m-isomers show high-frequency shifts though the p-isomer shows a low-frequency shift. The magnitude of the NH frequency shifts is quite small ($\leq$32 cm^{-1}) in all the aniline derivatives observed.

In the case of o-substituted aniline derivatives, intramolecular hydrogen bond formation is expected between the amino group and the neighboring substituent. As seen in Figure 1, however, the ν_s and ν_a bands of the o-isomers are very close to those of the m- and p-isomers of the same substituent, representing no clear indication of intramolecular hydrogen bond, such an extraordinarily large low-frequency shift of the NH bands, which was observed in the case of the OH bands of phenol derivatives.[4,6] Detailed examination on intramolecular hydrogen bonds will be described in section IV.C together with the presentation of IR spectra of deuterated isotopomers.

C. IR Spectra in D_0. The NH stretching vibrational region of aniline and its derivatives in D_0 is shown in Figure 2. The ADIR spectroscopy is applied to measure the IR spectra of the cations. Despite the IR spectra in S_0, ADIR spectra of *p*-cyanoaniline and *o*-methoxyaniline in D_0 were not obtained, because the Franck−Condon factor to the vibrational ground level in their D_0 is so small that enough number of the molecules cannot be pumped to their high Rydberg states.

Similar to the spectra in S_0, two bands in all the IR spectra in D_0 are easily assigned to ν_s and ν_a; those of the aniline cation are seen at 3393 and 3486 cm^{-1}, respectively, and the corresponding bands of the m- and p-substituted aniline cations are very close to those of the aniline cation. With respect to the NH frequency shifts due to the substituent in the cations, it is noticed that the directions of the shifts are opposite to those in S_0. The NH frequencies of the *m*- and *p*-methylanilines, *p*-fluoroaniline, and *p*-methoxyaniline cations show the high-frequency shifts, while those of the *m*-fluoroaniline and *m*-cyanoaniline cations shifted to the low-frequency side. It is also worth noting that the magnitude of the shifts in D_0 due to the substitution is rather smaller than those in S_0.

Among the o-substituted aniline cations, where intramolecular hydrogen bond formation is expected, the ν_s and ν_a bands of the *o*-cyanoaniline cation show remarkable NH frequency shifts from those of the aniline cation. The magnitude of the shifts is −53 and −35 cm^{-1} for ν_s and ν_a, respectively, and they are much larger than those of the *m*-cyanoaniline cation. The *o*-fluoroaniline cation also shows a low-frequency shift, but the magnitude is much smaller than the *o*-cyanoaniline cation. On the other hand, the ν_s and ν_a bands of the *o*-methylaniline cation shift to the high-frequency side similar to those of the m- and p-isomer cations. Such a remarkably large NH frequency shift in the *o*-cyanoaniline cation is regarded as a clear indication of the intramolecular hydrogen bond of the amino group with the neighboring cyano group. Further discussion based on the deuterated isotopomers will be described in section IV.C.

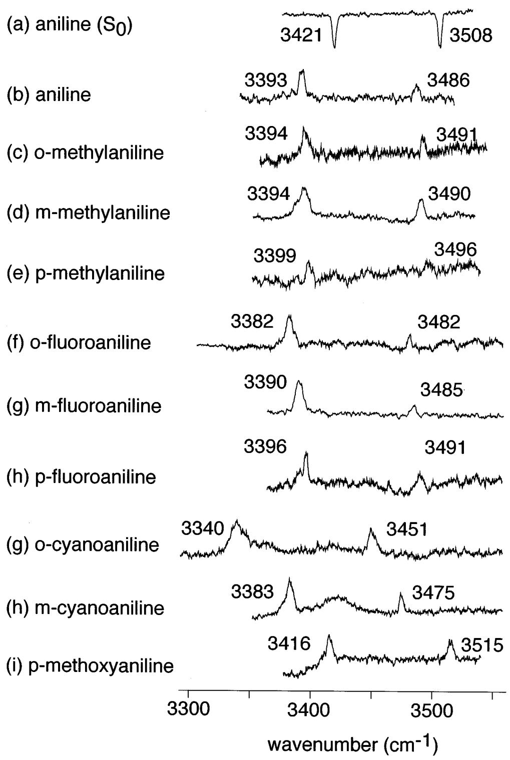

Figure 2. NH stretching vibrational region of IR spectra of (b) aniline and (c−i) monosubstituted anilines in the cationic ground state (D_0). The ADIR spectroscopic technique is used to measure the spectra. Spectrum a is the IR spectrum of aniline in S_0 reproduced for comparison.

D. DFT Calculations of Vibrational Spectra. To obtain structural information on aniline and its derivatives in S_0 and D_0, DFT calculations are carried out, and their reliability is examined by the comparison between the observed and calculated IR spectra of the NH stretching vibration. The energy optimized structures of aniline, methylaniline, fluoroaniline, and cyanoaniline in S_0 and D_0 are calculated at the B3LYP/6-31G-(d, p) level,[51] and their IR spectra in the NH stretch region are simulated on the basis of the energy-optimized structures with the harmonic approximation. All the calculations are carried out by using the Gaussian 98 program package.[52] Figure 3 shows the comparison between the observed and simulated IR spectra. In the simulated spectra, the scaling factors of 0.957 and 0.953 are applied to all the calculated NH stretching frequencies in S_0 and D_0, respectively. These scaling factors are determined for the calculated NH frequencies of aniline to be fitted to the observed ones. The simulated IR spectra reproduce well the observed spectra, especially the tendency of the NH frequency shifts depending on the substituents in both S_0 and D_0. Therefore, we conclude that this level of calculations gives us quantitatively reliable structural information.

IV. Discussion

A. NH Stretching Vibrations in the Aniline Cation. The ν_s and ν_a bands of aniline in D_0 appear at 3393 and 3486 cm^{-1}, respectively. Both ν_s and ν_a show the low-frequency shifts upon

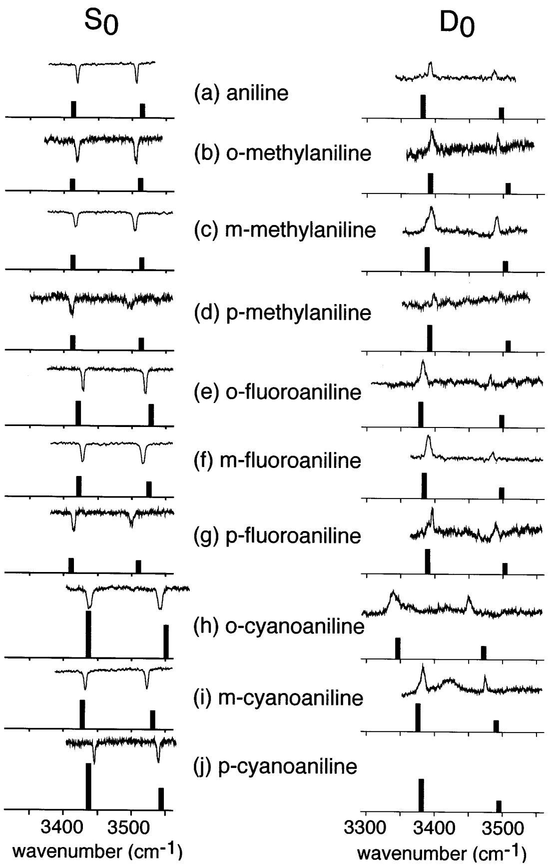

Figure 3. Comparison between the observed and simulated IR spectra of (a) aniline and (b−j) substituted anilines in (left) S_0 and (right) D_0. The simulated spectra are represented as bar graphs under the observed ones. The calculation level for the spectral simulation is B3LYP/6-31G(d,p). In the simulated spectra, the scaling factors of 0.957 and 0.953 are applied to all the calculated NH stretching frequencies in S_0 and D_0, respectively.

ionization, and the shifts are −28 and −22 cm^{-1}, respectively. These frequency shifts are somewhat surprisingly small in respect of the significant structural change (the nonplanar structure to the planar structure) of the amino group upon the ionization.[11−14] This behavior of the NH group is in contrast to that of the hydroxyl group in phenol, whose OH stretching vibrational frequency shows a low-frequency shift of 123 cm^{-1} upon ionization.[1,4] Both of the amino and hydroxyl groups are strongly conjugated with the aromatic π-bonds in aniline or in phenol. In the case of phenol, the low-frequency shift of the OH frequency associated with ionization is explained in terms of the mixing of the quinoid character, in which the electrons in the O−H bond are transferred to form the C=O bond.[7,53] Such small shifts of the NH stretches upon ionization suggest the conjugation of the amino group is not so extensive in D_0 as was found for the hydroxyl group.

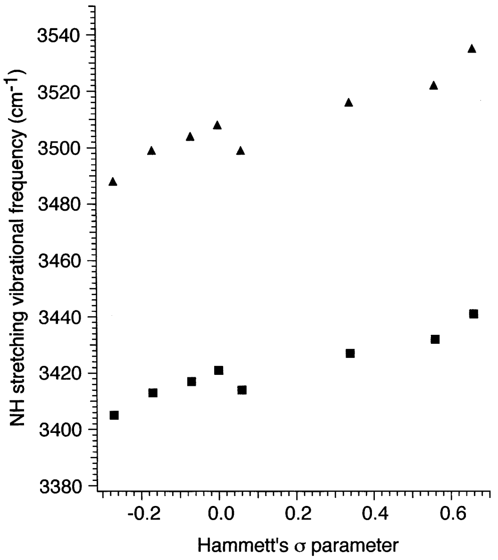

Figure 4. Plot of the NH stretching vibrational frequencies of m- and p-substituted anilines in S_0 vs Hammett's σ parameters of the substituents: (■) symmetric NH stretching vibration; (▲) antisymmetric NH stretching vibration. The σ parameters are taken from ref 56. Note the presence of a *positive* correlation between the NH frequencies and the σ parameter (see text).

The ν_s and ν_a frequencies of the bare aniline cation have been estimated by those of the aniline−Ar cation. Nakanaga et al. reported that the aniline−Ar cluster cation produced by REMPI of the neutral cluster shows the ν_s and ν_a bands at 3394.5 and 3488 cm^{-1}, respectively.[15] On the other hand, Solcà and Dopfer prepared the cluster ions by using a pick-up type ion source and observed NH bands at 3381 and 3477 cm^{-1}, respectively.[25] The NH frequency shifts from the bare aniline cation are only 1.5 and 2 cm^{-1} in the former case but are −12 and −9 cm^{-1} in the latter case. The difference of the NH frequencies is attributed to the difference of the cluster structures which depends on the preparation methods.[25] The REMPI production method results in the π-bonded cluster cation, in which Ar is located on the aromatic ring. On the basis of the present result, it is concluded that the perturbation from the Ar atom to the NH group is essentially negligible in such a π-bonded structure. On the other hand, the pick-up type ion source prepares cluster ions predominantly in the most stable structure.[25,26,37] The hydrogen-bonded structure, in which Ar is bound to the H atom of the amino group, is estimated as the most stable form of the cluster. The much larger NH frequency shifts from the bare cation are direct evidence for the production of the hydrogen-bonded structure. Such a presence of structural isomers in Ar cluster cations demonstrates that the "messenger" technique to determine vibrational frequencies of molecular cations has to be carefully used for spectroscopic evidence in the structure analysis.[5,35−37]

B. Substitution Effects on the NH Stretching Vibrations in the m- and p-Substituted Anilines. The ν_s and ν_a bands of substituted anilines show characteristic frequency shifts from those of aniline both in S_0 and D_0. In the case of the m- and p-substitution, intramolecular hydrogen bond formation is not geometrically possible. The NH frequency shifts due to the m- and p-substitution are, then, attributed to electronic effects by the substitution through the valence bond. Such a substitution effect on the stretching frequency has been also observed for the OH stretching vibrations of jet-cooled phenol derivatives.[7] In the case of the OH stretch, the frequency shift due to the substituent is quite small in the neutral (<10 cm^{-1}) but is remarkably enhanced upon the ionization (up to 70 cm^{-1}). No such drastic enhancement of the frequency shift is found for the NH stretch, but the moderate frequency shifts (<35 cm^{-1}) occur in both S_0 and D_0.

As for aniline derivatives in S_0, a positive correlation between the NH frequency shift and the Hammett's σ parameter of the substituent has been reported on the basis of IR spectroscopy in CCl_4 solutions.[54,55] The present jet-cooled IR spectra also support the previous result in the bulk study. A plot of the NH frequencies of jet-cooled substituted anilines in S_0 vs the Hammett σ values of the substituents is shown in Figure 4. In this plot, the σ values are taken from ref 56, and the NH

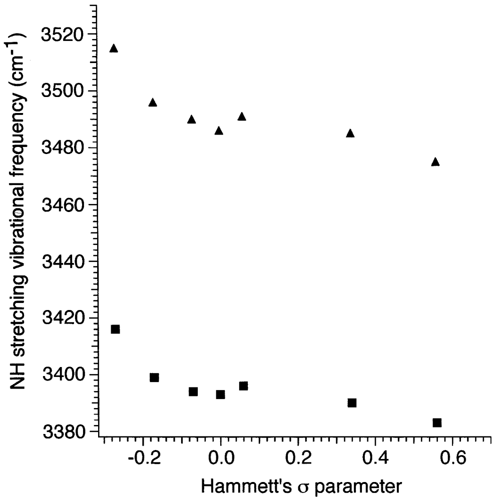

Figure 5. Plot of the NH stretching vibrational frequencies of m- and p-substituted anilines in D_0 vs Hammett's σ parameters of the substituents: (■) symmetric NH stretching vibration; (▲) antisymmetric NH stretching vibration. Note the presence of a *negative* correlation between the NH frequencies and the σ parameter (see text).

frequencies of o-substituted anilines are excluded to avoid the perturbation due to the intramolecular hydrogen bond. A positive correlation is clearly seen for both the NH symmetric and antisymmetric stretching vibrations; the stronger electron-withdrawing group causes the larger high-frequency shift while the stronger electron-donating group induces the larger low-frequency shift. On the other hand, the substitution effect in the cations is in sharp contrast to that in the neutrals. Figure 5 shows a plot of the NH frequency in the cations vs the Hammett σ of the substituent. The o-substituted anilines are excluded also in this plot. In the case of the cations, the plot indicates a clear *negative* correlation for both the NH symmetric and antisymmetric vibrations; the stronger electron-withdrawing group causes the larger low-frequency shift while the stronger electron-donating group induces the larger high-frequency shift.

A simple explanation can be given for the negative correlation in the cations. When aniline is ionized, the positive charge in the aromatic ring attracts the valence electrons in the N—H bonds into the ring, resulting in the reduction of the force field of the N—H bond, i.e., the low-frequency shifts of the NH frequency. The substitution by an electron-withdrawing group increases the positive charge on the ring and enhances the weakening of the N—H bond, while the electron-donating group decreases the positive charge and reduces the low-frequency shift upon the ionization. In the valence bond picture, such a transfer of the electron density from the N—H bond to the aromatic ring (increase of the positive charge on the amino group) can be interpreted as an increase of the sp^2 (quinoid) character of the amino group.

On the other hand, the positive correlation in S_0, which has already reported in the bulk study, has also been attributed to enhancement of the sp^2 character with increase of the positive charge on the amino group.[54,55] However, the present study clearly demonstrates that increase of the positive charge in the amino group, and the resulting sp^2 hybridization should cause a low-frequency shift of the NH vibration, as seen in the cations. The conventional explanation for the positive correlation in S_0 is highly questionable when we refer the NH frequencies in the cations. At the present stage, it is difficult to give a simple explanation to the substitution effect in S_0.

C. Intramolecular Hydrogen Bond in o-Substituted Anilines. In the case of o-substituted anilines, intramolecular hydrogen bond formation between the amino group and the neighboring substituent is expected. Prior to examination of the observed IR spectra of the NH stretching vibrations, here we first discuss spectral indications for intramolecular hydrogen bond formation of the amino group.

In the aniline cation, the symmetric (ν_s) and antisymmetric (ν_a) NH stretching modes are expressed as a linear combination of the two NH local oscillators, which are degenerated in the zero-order approximation. The two local oscillators are equivalent so that the energy splitting between the two modes would be quite symmetric with respect to the degenerated zero-order energy. On the other hand, in o-substituted anilines, in which an intramolecular hydrogen bond is expected, one of the two NH local oscillators interacts with the proton-accepting group through intramolecular hydrogen bond formation, so that the frequency reduction takes place only for the interacting local oscillator. Thus, the degeneracy is lifted, and the energy of the other oscillator is left unchanged. Finally, the coupling between the two nonequivalent oscillators leads to a minor splitting, and we also call the resulting modes the symmetric and antisymmetric NH vibrations, although the contributions of the two NH local oscillators are not evenly weighted; the symmetric NH stretch contains more the hydrogen-bonded NH component, while the free NH contributes more to the antisymmetric NH stretch. An important feature of the intramolecular hydrogen bond formation in substituted anilines is that the magnitude of the frequency reduction is no longer to be equal for the symmetric and antisymmetric NH stretches; the symmetric stretch shows a larger low-frequency shift than the antisymmetric NH stretch.

In this study, we examined the NH stretching vibrations in S_0 of four o-substituted anilines, as seen in Figure 1; however, no one shows a distinct low-frequency shift of the NH bands with respect to the band positions of aniline. Moreover, the o-isomers tend to show rather slightly higher NH frequencies than the corresponding m- and p-isomers. The results suggest that the intramolecular hydrogen bond is not formed or is extremely weak in these aniline derivatives in S_0. The perturbation on the NH vibrations from the o-substituents is so small that the frequency shift is totally canceled by more remarkable substituent effects through the valence bonds. These results on the aniline derivatives are in sharp contrast to neutral o-substituted phenols.[4,57,58] The OH stretching vibrations in *o*-fluorophenol, *o*-methoxyphenol, and *o*-cyanophenol show the low-frequency shifts of 26, 60, and 71 cm^{-1}, respectively, due to the intramolecular hydrogen bond formation. The much lower proton-donating ability of the amino group than the hydroxyl group is responsible for the absence of the apparent low-frequency shift in o-substituted anilines in S_0. The nonplanar structure of the amino group in S_0 provides a poor spatial overlap between the amino proton and the electron cloud of the acceptor, and it also inhibits a firm formation of an intramolecular hydrogen bond.

Though only *o*-methylaniline shows very small low-frequency shifts in S_0 among the o-substituted anilines, it would be attributed to the electronic effect through the aromatic ring; the proton acceptability of the methyl group is extremely low so that no hydrogen bond formation in S_0 is expected.[3,6] The larger low-frequency shifts in the m- and p-isomers support this interpretation.

As for the o-isomers in D_0, we observed the NH stretches in *o*-methyl, *o*-fluoro, and *o*-cyanoaniline. Both of the ν_s and ν_a bands of the *o*-cyanoaniline cation show remarkable low-frequency shifts with respect to the corresponding bands of the

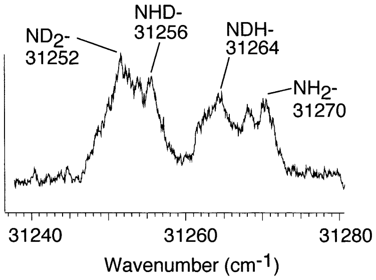

Figure 6. Origin band region of the S_1−S_0 transition of deuterated isotopomers of *o*-cyanoaniline (see text).

aniline cation, and their frequency shifts are more prominent for ν_s ($\Delta\nu_s = -53$ cm^{-1}) than for ν_a ($\Delta\nu_a = -35$ cm^{-1}). Such a characteristic behavior of the *o*-cyanoaniline cation strongly suggests intramolecular hydrogen bond formation between the amino and cyano groups. The *o*-fluoroaniline cation also shows low-frequency shifts of the NH frequencies. Though the shifts are much smaller than those of the *o*-cyanoaniline cation, it shows the similar feature that the frequency reduction is larger for ν_s ($\Delta\nu_s = -11$ cm^{-1}) than for ν_a ($\Delta\nu_a = -4$ cm^{-1}). In the case of the *o*-methylaniline cation, the NH frequencies are slightly high-frequency shifted than those of the aniline cation, and no clear indication of the intramolecular hydrogen bond formation is seen.

Though the large NH frequency shifts of the *o*-cyanoaniline cation strongly suggest the intramolecular hydrogen bond formation, electronic effects due to the substitution through the chemical bonds also can contribute to the shifts; a strong electron-withdrawing cyano group may cause the similar low-frequency shifts in D_0, as discussed in section IV.B. To find which factor is more important for the NH frequency reduction, we carried out the observation of deuterated isotopomers of the *o*-cyanoaniline cation. Shown in Figure 6 is the origin band region for the S_1−S_0 transition of deuterated isotopomers of *o*-cyanoaniline. Because of the partial deuteration of the amino group, four bands corresponding to the NH_2-, NDH-, NHD-, and ND_2-isotopomers appear in the spectrum. Here, the *NDH*-isotopomer represents that the H atom is sitting at the trans position with respect to the cyano group, while the *NHD*-isotopomer means that the H atom is at the cis position to the cyano group. These assignments of the isotopomer bands are based on the IR spectra as described below.

IR spectra of the isotopomers of cyanoaniline in S_0 and D_0 are shown in Figure 7. When one of the H atoms in the amino group is deuterated, the coupling between the NH and ND local oscillators is known to be practically negligible because of a large frequency difference between these two oscillators,[59] so that the observed NH frequency can be regarded as the frequency of the local oscillator itself. Therefore, the NH frequency of the NDH-isotopomer reflects only the electronic effect of the cyano substitution through the aromatic ring, and that of the NHD isotopomer is affected by both the electronic effect and the intramolecular hydrogen bond. Because the electronic effect through the aromatic ring should be common in the NHD- and NDH-isotopomers, the difference between the NH frequencies of the NHD- and NDH-isotopomers represents the contribution due to the intramolecular hydrogen bond formation.

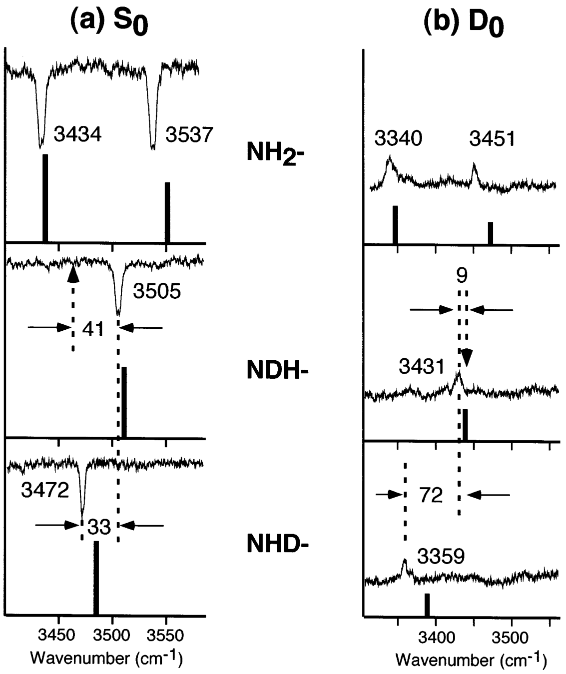

Figure 7. IR spectra of the deuterated isotopomers of *o*-cyanoaniline in (a) S_0 and (b) D_0. The bar graphs under the observed spectra are simulated IR spectra at B3LYP/6-31G(d,p). In the simulated spectra, the scaling factors of 0.957 and 0.953 are applied to all the calculated NH stretching frequencies in S_0 and D_0, respectively. Vertical arrows seen in the spectra of the NDH-isotopomer indicate the averaged frequency of the symmetric (ν_s) and antisymmetric (ν_a) NH stretching vibrations of aniline.

The NH stretch bands of the NHD- and NDH-isotopomers of the *o*-cyanoaniline cation are found at 3359 and 3431 cm^{-1}, respectively. The NH frequency difference of 72 cm^{-1} can be regarded as the frequency shift due to the intramolecular hydrogen bond. The NH frequency of the NDH-isotopomer cation shows a low-frequency shift of 9 cm^{-1} from the average frequency of the ν_s and ν_a bands of the aniline cation (3440 cm^{-1}), and this shift is attributed to the substitution effect through the aromatic ring. An interesting feature is that the NH stretch bands of the NHD- and NDH-isotopomers of *o*-cyanoaniline exhibit different frequencies even in S_0; the NH stretch band of the NHD-isotopomer is found at 3472 cm^{-1}, while that of the NDH-isotopomer appears at 3505 cm^{-1}. This means that the intramolecular hydrogen bond is actually formed even in S_0, and the low-frequency shift due to the hydrogen bond is so small that it is hidden by the high-frequency shift due to the electronic effect. The shifts due to the hydrogen bond and substitution effect are evaluated to be −33 and +41 cm^{-1}, respectively, by the same estimation method of the shift as the cation. The NH frequency shift due to the intramolecular hydrogen bond becomes about twice upon ionization, indicating a remarkable enhancement of the hydrogen bond strength in D_0. This enhancement of the hydrogen bond strength is mainly attributed to the increase of the positive charge on the amino group. The similar enhancement of the hydrogen bond strength has been observed in various o-substituted phenols.[2−4,6] In the case of *o*-cyanoaniline, the structural change of the amino group from the nonplanar to the planar form also contributes to the enhancement because the latter form provides a better spatial overlap between the amino proton and the π-electron cloud of the cyano group.

Theoretical calculations also support the distinction between the hydrogen bonding and the electronic substitution effect obtained from the experimental results on the deuterated isotopomers. The simulated IR spectra of the isotopomers at B3LYP/6-31G(d,p) are also shown in Figure 7 together with the observed ones. The scaling factors of 0.957 and 0.953 are applied for the calculated frequencies in S_0 and D_0. These scaling factors are determined for the best fit in aniline, as described in

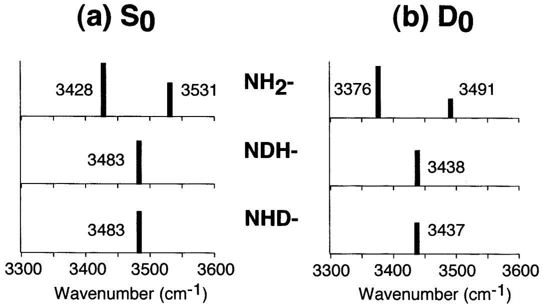

Figure 8. Simulated IR spectra of the NH stretching vibrations in deuterated isotopomers of *m*-cyanoaniline in (a) S_0 and (b) D_0. The calculation level is B3LYP/6-31G(d,p). The scaling factors of 0.957 and 0.953 are applied to all the NH stretching frequencies in S_0 and D_0, respectively.

section III.D. The NH frequency differences between the NHD- and NDH-isotopomers are clearly reproduced by the calculations for both the S_0 and D_0 states. For comparison, the same level of calculations are also carried out for deuterated isotopomers of *m*-cyanoaniline, where intramolecular hydrogen bond formation is not feasible due to the geometrical restriction, and we confirm that the NHD- and NDH-isotopomers of *m*-cyanoaniline show no NH frequency difference, as seen in Figure 8. These calculations clearly demonstrate that the NH frequency difference between the NHD- and NDH-isotopomers of *o*-cyanoaniline is attributed to the intramolecular hydrogen bond.

As seen in Figures 3 and 7, the B3LYP/6-31G(d,p) calculations reproduce well the characteristic low-frequency shifts of the NH stretches in *o*-cyanoaniline, indicating that the energy-optimized structure at this calculation level is reliable enough to discuss the intramolecular hydrogen bond. In Figure 9a,b are displayed key geometrical parameters of the energy-optimized structures for *o*- and *m*-cyanoaniline in S_0 and D_0 (the parameters in D_0 are seen in parentheses).[60] In both the o- and m-isomers, the nonplanar amino group in S_0 and the planar structure in D_0 are also reproduced, and the N−H bond length is extended in both the species upon ionization. The intramolecular hydrogen bond formation should result in the longer N−H bond distance. In the S_0 o-isomer, the "cis" N−H bond length (r_b) is 0.21 pm longer than the "trans" N−H bond length (r_a). The asymmetry of the N−H bond lengths becomes more significant upon ionization; the cis N−H length is 0.34 pm longer than the trans N−H. This shows a sharp contrast to the case of the m-isomer, where the cis and trans N−H lengths are almost identical ($r_a - r_b = 0.01$ pm) in both S_0 and D_0, and it supports that the intramolecular hydrogen bond does exist in the o-isomer. The CNH angles (∠a and ∠b in Figure 9a,b) also show an indication of the intramolecular hydrogen bond. In accordance with the increase of the intramolecular hydrogen bond strength upon ionization, ∠b becomes much smaller than ∠a in D_0. This suggests that the cyano group attracts more strongly the cis H atom in the cation. The distance between the cis proton and the cyano group (r_c) is remarkably reduced upon ionization. This is mainly attributed to the structural change of the amino group from the nonplanar to the planar form. This change also contributes to the enhancement of the intramolecular hydrogen bond strength upon ionization.

In the intramolecular hydrogen bond of *o*-cyanoaniline, the π-electrons of the cyano group accept the proton of the amino group. Such a π-hydrogen bond is generally much weaker than conventional σ-hydrogen bonds, and it is somewhat unexpected that the remarkable intramolecular hydrogen bond is formed in cyanoaniline. It has been, however, found for the neutral ground state that the OH stretching frequency of *o*-cyanophenol (3586 cm^{-1}) is lower than that of *o*-methoxyphenol (3599 cm^{-1}), whose substituent is a typical proton acceptor having lone pair electrons.[4,57] The low-frequency shifts of the OH vibration of these molecules from that of phenol (3657 cm^{-1}) can be mainly attributed to the intramolecular hydrogen bond. Therefore, it is concluded that *o*-cyanophenol forms a stronger intramolecular hydrogen bond than *o*-methoxyphenol, indicating the strong proton acceptability of the cyano group rather than the methoxy group.

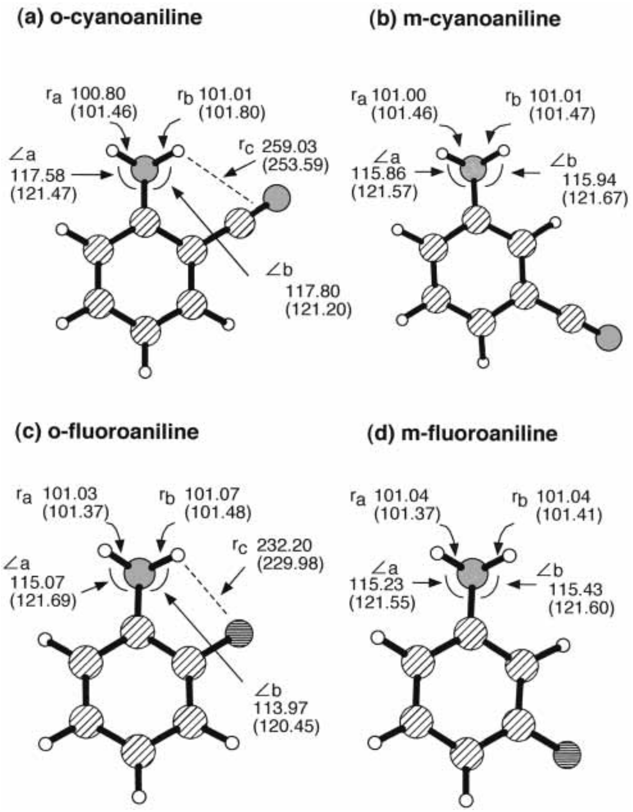

Figure 9. Key structural parameters of energy optimized structures at B3LYP/6-31G(d,p) for (a) *o*-cyanoaniline, (b) *m*-cyanoaniline, (c) *o*-fluoroaniline, and (d) *m*-fluoroaniline in S_0 and D_0. Values in the parentheses are parameters in D_0. Units of the bond distances and angles are pm and degree, respectively.

The NH stretching vibrations of *o*-fluoroaniline show the similar behavior to those of *o*-cyanoaniline upon ionization, though the magnitude of the frequency shifts is much smaller for *o*-fluoroaniline. Such characteristic NH frequency shifts strongly suggest the presence of the intramolecular hydrogen bond with the neighboring fluorine atom. The optimized structure of *o*-fluoroaniline at B3LYP/6-31G(d,p) is illustrated in Figure 9c, and it clearly shows asymmetry between the N−H bond lengths; the cis N−H length is longer than the trans N−H length. Though the asymmetry is quite small in S_0, it is remarkably enhanced upon ionization. This is consistent with the observed IR spectra, where the spectrum in S_0 shows no clear evidence of the intramolecular hydrogen bond, while the remarkable low-frequency shifts occur in D_0. For comparison, the optimized structure of *m*-fluoroaniline is also presented in Figure 9d. The two N−H bond lengths are quite similar in both S_0 and D_0, indicating that the lengths of the cis and trans N−H bonds should be practically identical with no effect of intramolecular hydrogen bond formation.

In our previous IR study of cresol (methylphenol), we found that an unconventional intramolecular hydrogen bond between the methyl and hydroxyl groups is created upon ionization.[3,6] The OH stretching vibrations of o-, m-, and p-isomers of cresol in S$_0$ show no significant difference in frequency. However, only the OH band of the o-isomer cation exhibits a distinct low-frequency shift of 25 cm^{-1} from those of other isomer cations, representing the presence of the intramolecular hydrogen bond. These results indicate that the methyl group acts as an acceptor of the hydroxyl proton in the intramolecular hydrogen bond of the *o*-methylphenol cation. The similar OH frequency shift characteristic only in the o-isomer cation was also found in ethylphenol.[6] Though the nature of this unconventional intramolecular hydrogen bond, i.e., the proton acceptability of the alkyl group in the aromatic cations, is still under a controversial issue,[8,9,61−63] interaction between the amino and methyl groups in the *o*-methylaniline cation is quite interesting with respect to the understanding of the unconventional hydrogen bond found in the alkylphenol cations. However, the NH stretches in the *o*-methylaniline cation show only small high-frequency shift compared with the NH stretches in the aniline cation, and no clear evidence for such an intramolecular hydrogen bond is found. The proton-donating ability of the amino group is much lower than that in the hydroxyl group, and the low-frequency shift due to the unconventional hydrogen bond might be totally hidden by the larger high-frequency shift caused by the electronic substitution effect through the aromatic ring, even if it is also formed in the *o*-methylaniline cation.

V. Concluding Remarks

In this work, we applied IR spectroscopy to jet-cooled aniline and substituted anilines and determined their precise NH stretching frequencies in both S$_0$ and D$_0$. The NH frequency of the aniline derivative in S$_0$ shows a positive correlation with the Hammett σ parameter of the substituent. Upon ionization, the NH frequency of the amino group shows the low-frequency shift whose magnitude depends on the substituent, representing a negative correlation with the σ parameter.

The NH frequency shifts in *o*-cyano- and *o*-fluoroaniline indicate the intramolecular hydrogen bond formation with the neighboring proton-accepting group. A remarkable enhancement of the intramolecular hydrogen bond strength upon ionization was found. Especially in the case of *o*-cyanoaniline, the IR spectra of the deuterated isotopomers gave us a clear evidence for the hydrogen bond formation. The DFT calculations reproduced well the observed NH frequency shifts, and the energy-optimized structures support the presence of the intramolecular hydrogen bond in these isomers. In both the *o*-cyanoaniline and *o*-fluoroaniline cations, the N−H bond extension due to the intramolecular hydrogen bond is extremely small, and its magnitude is estimated to be 0.1−0.3 pm in the DFT calculations. The present experimental results demonstrate the high potential of IR spectroscopy to probe extremely weak intramolecular hydrogen bonds in cations.

Acknowledgment. The authors greatly acknowledge Dr. H. Ishikawa and Dr. T. Maeyama in Tohoku university for helpful discussion.

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