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Infrared spectroscopy of the phenol-N₂ cluster in S₀ and D₀: Direct evidence of the in-plane structure of the cluster

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The OH stretching vibration of jet-cooled phenol-N₂ in the neutral and cationic ground states was observed by using infrared-ultraviolet double resonance spectroscopy and infrared photodissociation spectroscopy, respectively. The OH vibration showed a small but significant low-frequency shift of 5 cm⁻¹ upon the cluster formation in the neutral, while the shift drastically increased up to 159 cm⁻¹ in the cation. These results represent the direct evidence of the in-plane cluster structure, in which phenolic OH is hydrogen bonded to N₂, as was proposed in the zero kinetic energy photoelectron study [S. R. Haines *et al.*, J. Chem. Phys. **109**, 9244 (1998)]. © 1999 American Institute of Physics. [S0021-9606(99)02023-1]

I. INTRODUCTION

Microscopic solvation of an aromatic molecule with nonpolar solvent molecules has been subjected to various spectroscopic studies of clusters in supersonic jets.¹ Many of such studies were concerned with the solvation with rare gas atoms, and it was found that the first step of the solvation usually takes place at the π system of the aromatic ring, being subjected to the van der Waals force. Even in the case of the solvation of phenol with rare gas atom such as Ar, in which the hydroxyl group is known to be a substantially interactive site, it has been strongly suggested that the rare gas atom prefers to attach on the aromatic ring rather than on the hydroxyl group.^{2,3}

On the other hand, our knowledge on microscopic solvation of aromatics by other nonpolar molecules is scarce.⁴ Recently, Haines *et al.* have reported the S₁-S₀ electronic and zero kinetic energy (ZEKE) photoelectron spectra of phenol-N₂. They found that the binding energy of the cluster is 445 and 1650 cm⁻¹ in the neutral (S₀) and cationic (D₀) ground states, respectively.⁵ The binding energy of the cluster, especially in D₀, is much larger than those of typical van der Waals clusters of aromatic molecules with rare gas atoms (≤ 400 cm⁻¹ in S₀ and ≤ 600 cm⁻¹ in D₀).¹ With the help of high level *ab initio* calculations, Haines *et al.* concluded that an in-plane structure for the cluster is feasible both in S₀ and D₀, in which phenolic OH is bound to the lone pair of electrons of the nitrogen molecule.⁵ This is of rather unexpected structure with respect to the out-of-plane structure of benzene-N₂ and phenol-Ar, in which the solvent locates on the aromatic ring.^{2,3,6}

In this communication, we report infrared (IR) spectra of jet-cooled phenol-N₂ in the OH stretching vibrational region. The IR spectra were observed in S₀ and D₀ by using infrared-ultraviolet double resonance spectroscopy and infrared photodissociation spectroscopy, respectively. The OH frequency of phenol-N₂ was compared with those of bare phenol and phenol-Ar. While the cluster formation with Ar

causes an almost negligible shift of the OH frequency both in S₀ and D₀, a large frequency shift was found to occur for phenol-N₂, especially in D₀. These results indicate that the N₂ molecule is bound to the OH site to reduce the force field of the hydroxyl group, providing the direct evidence for the hydrogen-bonded structure proposed by Haines *et al.*⁵

II. EXPERIMENT

The infrared-ultraviolet (IR-UV) double resonance and infrared photodissociation (IRPD) spectroscopic techniques were utilized to observe the OH stretching vibration of phenol-N₂ in S₀ and D₀, respectively. The details of both the techniques are described elsewhere.^{7,8} Only a brief description is given here.

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

A pulsed UV laser whose wavelength is fixed to the origin band of the S₁-S₀ transition of the species selected is introduced, and the resonance enhanced multiphoton ionization (REMPI) signal is observed as a measure of its ground state population. Prior to the UV laser, and IR laser pulse is introduced, and its wavelength is scanned. When the IR wavelength is resonant to the vibrational transition of the species, the IR absorption induces a reduction of the ground state population, resulting in depletion of the REMPI signal intensity.

B. IRPD spectroscopy for cluster cations

The cluster cation is produced by two-color photoionization of the neutral cluster to suppress the internal energy and to avoid the fragmentation of the cluster ion. The first UV laser excites the neutral cluster to the vibrational ground state of S₁, from which the second UV laser ionizes it to be slightly higher than the ionization threshold. After a delay-time of 50 ns from the UV pulse, the IR laser is introduced for the vibrational excitation. When the IR wavelength is resonant to the vibrational transition of the cluster ion, the vibrational excitation causes vibrational predissociation of the cluster ion, leading to depletion of the cluster ion inten-

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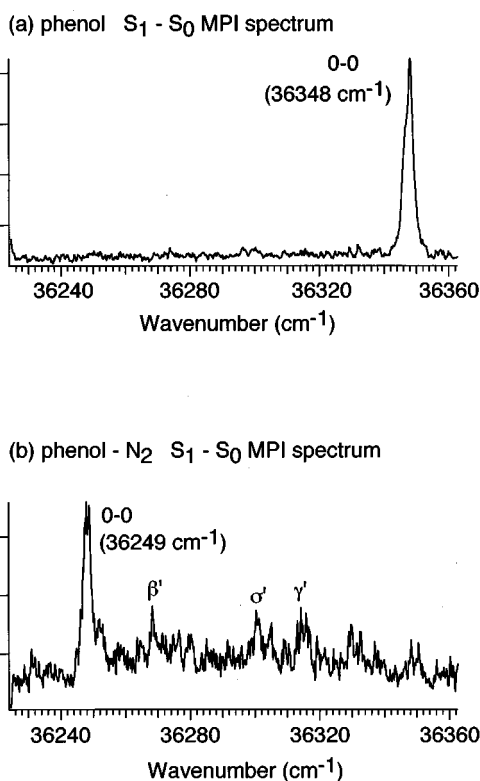


FIG. 1. REMPI spectra of the S_1 - S_0 transition of (a) bare phenol and (b) phenol- N_2 . The phenol ion ($m/e=94$) and the 1:1 cluster ion ($m/e=122$) were monitored, respectively. In the spectrum (b), two-color ionization (the ionization laser wavelength is fixed at 317.7 nm) was used to suppress the dissociation of the cluster ion.

sity. Thus, by scanning the IR wavelength while monitoring the cluster ion intensity, the IR spectrum of the cluster ion is obtained as the depletion spectrum.

The sample of phenol was kept at room temperature in a sample compartment, and its vapor was seeded in a 1:1 gaseous mixture of N_2 and Ar at 4 atm stagnation pressure. The gaseous mixture was expanded into a vacuum chamber through a pulsed nozzle. Typical background pressure of the chamber was 7×10^{-6} Torr. The jet expansion was skimmed by a skimmer of 1 mm diam, and the resulting molecular beam was introduced into the interaction region with the laser beams. A time-of-flight mass spectrometer of the Wiley-McLaren type was used for the mass separation of ions.

III. RESULTS AND DISCUSSION

A. OH stretching vibration of phenol- N_2 in S_0

Figure 1 shows the mass-selected S_1 - S_0 REMPI spectra of (a) bare phenol and (b) phenol- N_2 , in which the phenol ion ($m/e=94$) and the 1:1 cluster ion ($m/e=122$) were monitored, respectively. In the spectrum (b), we utilize the two-color ionization scheme, in which the first UV laser wavelength is scanned while the second UV laser is fixed at 317.7 nm. The excess energy upon the ionization is kept below 300 cm^{-1} when the origin band of S_1 is tuned, and this is very effective in excluding the dissociation of the cluster upon the ionization. The S_1 - S_0 electronic spectrum

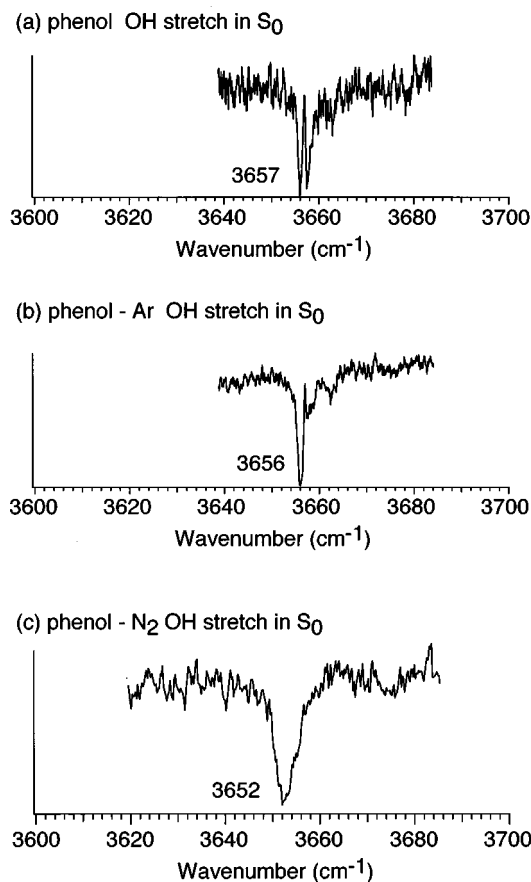


FIG. 2. OH stretching vibrational region of infrared spectra of jet-cooled (a) bare phenol, (b) phenol-Ar, and (c) phenol- N_2 in S_0 . The infrared-ultraviolet double resonance technique was used to measure the spectra. The band splitting in the spectra (a) and (b) is due to absorption of the infrared laser light by the atmospheric water in the optical path.

of phenol- N_2 has been reported by Haines *et al.*; its origin band appears at 36249 cm^{-1} , which is low-frequency shifted by 99 cm^{-1} from that of bare phenol.⁵ This shift is substantially larger than that of phenol-Ar (-33 cm^{-1}).² Three intermolecular vibrational bands (σ' : stretch, β' : in-plane bent, and γ' : in-plane wag) are seen in the spectrum in Fig. 1(b); details of the intermolecular vibrations in the electronic spectrum have been described in the article by Haines *et al.*⁵

Figure 2 shows the OH stretching vibrational region of the IR-UV double resonance spectra of (a) bare phenol, (b) phenol-Ar, and (c) phenol- N_2 in S_0 . In each spectrum, the UV laser frequency is fixed at the 0-0 band of the S_1 - S_0 transition of each species (36348 , 36315 , and 36249 cm^{-1} for bare phenol, phenol-Ar, and phenol- N_2 , respectively), while the IR wavelength was scanned. The OH stretch of bare phenol appears at 3657 cm^{-1} (Ref. 7), and that of phenol-Ar shows only 1 cm^{-1} low-frequency shift from the OH band of bare phenol. On the other hand, the OH band of phenol- N_2 occurs at 3652 cm^{-1} , being low-frequency shifted by 5 cm^{-1} from that of bare phenol. This behavior is clearly discriminated from the case of phenol-Ar.

The polarizabilities of N_2 and Ar are 1.7403 and $1.6411 \times 10^{-24} \text{ cm}^3$ (Ref. 9), and the proton affinities are 118.2 and 88.6 kcal/mol, respectively.¹⁰ In spite of similar molecular properties, the OH stretches of phenol- N_2 and

phenol-Ar show quite different behavior, suggesting different cluster structures. For phenol-Ar, the extremely small OH frequency shift upon the cluster formation indicates the out-of-plane structure, in which the Ar atom locates on the aromatic ring. In this structure, the perturbation from Ar to the force field of phenolic OH is expected to be very weak. A similar phenomenon has been reported for the NH stretches in aniline-Ar.¹¹

On the other hand, such a substantial low-frequency shift in phenol-N₂ suggests that the cluster formation with N₂ gives an essential perturbation to the phenolic OH force field. For phenol-N₂, an in-plane structure has been proposed by Haines *et al.*⁵ On the basis of *ab initio* calculations and intermolecular vibrational analysis, they predicted that phenolic OH is bound to the lone pair of electrons of the nitrogen molecule. This in-plane structure should cause a perturbation to the force field of the phenolic OH stretch than the out-of-plane structure, and it is consistent with the larger low-frequency shift observed in the present work.

Though the *ab initio* calculations of the cluster structure⁵ and experimentally observed OH frequency shift for phenol-N₂ strongly suggest the presence of the hydrogen bond, the shift of -5 cm^{-1} is much smaller than those found in typical hydrogen-bonded clusters of phenol, for example, -133 cm^{-1} for phenol-H₂O and -363 cm^{-1} for phenol-NH₃, which also have the in-plane structures.^{7,12} This fact indicates that the nature of the bond between phenol and N₂ would be an intermediate character between hydrogen bond and van der Waals bond. Such character of the intermolecular bond in phenol-N₂ is also suggested by its binding energy; the intermolecular binding energy of phenol-N₂ is estimated to be 445 cm^{-1} in *S*₀.⁵ This value is close to those of van der Waals bonds in *S*₀ (typically $\leq 400\text{ cm}^{-1}$), and is much smaller than those of typical hydrogen bonds of aromatic alcohol ($1000\text{--}3000\text{ cm}^{-1}$).^{1,13}

B. OH stretching vibration of phenol-N₂ in *D*₀

IRPD spectroscopy is very useful for cluster cations, since the vibrational excitation readily induces the dissociation of the intermolecular bond. This method, on the other hand, cannot be applied to bare molecular cations because of the difficulty in the dissociation of firm chemical bonds in the cations. Despite of this experimental difficulty, the OH stretching vibration of jet-cooled bare phenol in *D*₀ was recently measured by using a newly developed IR spectroscopic technique, autoionization-detected infrared (ADIR) spectroscopy. Details of ADIR spectroscopy are described elsewhere.^{3,14} Figure 3(a) shows the OH stretch region of the ADIR spectrum of the bare phenol cation. The OH stretch frequency in *D*₀ occurs at 3534 cm^{-1} .^{3,14} The IRPD spectra of the phenol-Ar and phenol-N₂ cations are shown in Figs. 3(b) and 3(c), respectively. In each spectrum, the cluster cation is produced by REMPI via the 0-0 band of the *S*₁-*S*₀ transition of the cluster. The spectrum of the phenol-Ar cation is reproduced from our previous letter.⁸ It is noticed that the OH frequency of the phenol-N₂ cation shows a remarkable low-frequency shift by $-159(\pm 5)\text{ cm}^{-1}$ from that of the bare phenol cation, while the shift of the phenol-Ar cation is almost negligible ($+1\text{ cm}^{-1}$).

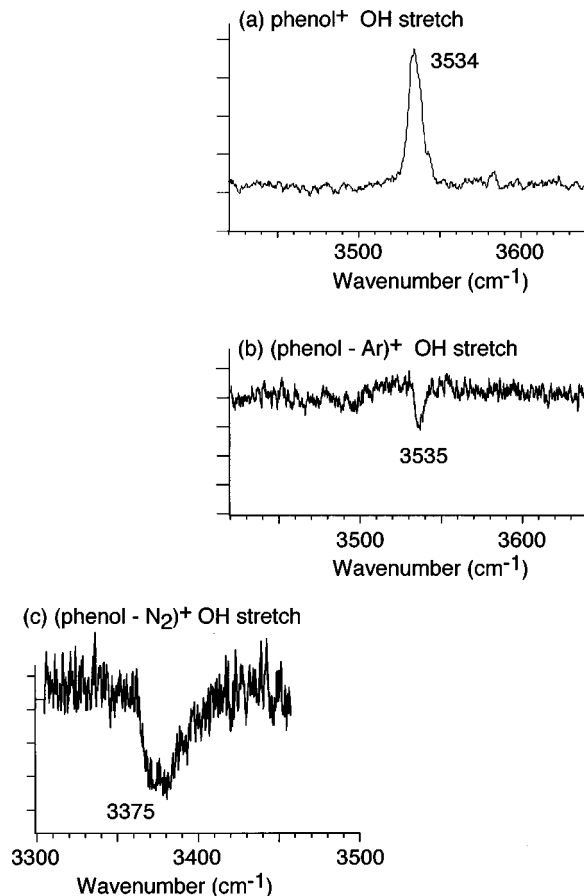


FIG. 3. OH stretching vibrational region of infrared spectra of (a) bare phenol, (b) phenol-Ar, and (c) phenol-N₂ in *D*₀. For the spectrum (a), the autoionization-detected infrared spectroscopy was used, while the infrared photodissociation technique was used for the spectra (b) and (c) (see text). Note that all the spectra are shown in the same frequency scale.

Such a contrast in the OH frequency shift upon the cluster formation should be related to the difference in the structures of the cluster cations. From the negligible OH frequency shift, the out-of-plane structure for phenol-Ar in *D*₀ is also inferred as in *S*₀.⁸ Though the interaction between the π system and Ar is expected to be enhanced upon ionization, no apparent effects on the OH frequency are found. Similar negligible frequency shifts are also known for the in-plane vibrations of other aromatic-Ar cluster cations, such as *p*-ethylphenol for the CH stretches¹⁵ and 2-naphthol for the OH stretch.¹⁶

On the other hand, the large OH frequency shift in the phenol-N₂ cation is an unequivocal evidence for the in-plane structure, in which phenolic OH is bound to the lone pair of electrons of N₂. This is consistent with the *ab initio* calculations for the cationic state and the ZEKE photoelectron study by Haines *et al.*⁵ The drastic increase of the frequency shift demonstrates a significant enhancement of the intermolecular bond strength between phenol and N₂ upon the ionization, and the hydrogen bond nature of the intermolecular bond is clear in the cation. This is also consistent with the dissociation energy measurement by Haines *et al.* (1650 cm^{-1} in *D*₀).⁵ Similar drastic change of the hydrogen bond strength has been reported for the phenol-benzene cation, where they are bound through π -hydrogen bond.¹⁷ In this case, the low-

frequency shift of phenolic OH due to the π -hydrogen bond is 78 cm^{-1} in S_0 , but is increased to 475 cm^{-1} in D_0 . These results clearly indicate that even a “weak” hydrogen bond in neutral species can become a “strong” hydrogen bond upon ionization.

IV. CONCLUSION

In this communication, we reported the OH stretch region of the IR spectra of phenol- N_2 both in S_0 and D_0 . In both states, the OH frequency shows distinct low-frequency shifts from that of bare phenol, and comparison with those of phenol-Ar gives us the direct evidence for the in-plane structure of phenol- N_2 , which has been proposed by Haines *et al.* based on the *ab initio* calculations and intermolecular vibrational analysis.⁵ The intermolecular bond of phenol- N_2 can be regarded as an intermediate between hydrogen bond and van der Waals bond in S_0 , but it shows more obvious hydrogen bond nature in D_0 . This is a typical example of a drastic enhancement of hydrogen bond strength upon ionization.

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