A Molecular Cluster Study on Activated CH/π Interactions: Infrared Spectroscopy of Aromatic Molecule−Acetylene Clusters

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Received: January 6, 2004; In Final Form: February 5, 2004

CH stretching vibrations of jet-cooled benzene−acetylene and several aromatics−acetylene clusters were observed in order to characterize the intermolecular interaction, so-called activated CH/π interaction between an acidic CH group and π-electrons. The infrared−ultraviolet double resonance spectroscopic techniques were used for measuring their vibrational spectra. The antisymmetric CH stretching vibration of the acetylene moiety exhibits a remarkable low-frequency shift upon the cluster formation with the aromatic molecules, indicating such a cluster structure that the acetylenic CH group is bound to π-electrons of the aromatic ring. The low-frequency shifts observed for the clusters show a positive correlation with the π-electron density of the ring, as expected for an ordinary π-hydrogen bond. On the other hand, the polarizability of the proton-accepting molecules showed a weakly negative correlation with the CH frequency shifts. These results show that the intermolecular interaction between the activated CH group and π-electrons is characterized as a π-hydrogen bond rather than as a van der Waals interaction.

I. Introduction

Acidity of a CH group is generally much weaker than those of conventional proton donors such as OH and NH groups, so that much interest has been attracted to the presence of hydrogen bonds between a CH group and various proton acceptors.[1−3] Such a hydrogen bond between a CH group and a hard base molecule having lone pair electrons is now widely known, though its several unconventional characters, such as high-frequency shifts of CH stretching vibrations, have been found.[4−7] On the other hand, Nishio and co-workers first pointed out the nature of a weak and attractive interaction between a CH group and π electrons, on the basis of the preferential contact between the bulky alkyl and phenyl groups, and they called it “CH/π interaction”.[8] Despite its extremely weak interaction energy ($<$2.5 kcal/mol), the reality of this interaction has been supported by experimental evidence, and this interaction is supposed to play a key role in crystal packing and molecular recognition.[8−13] The nature of the CH/π interaction is, however, still very controversial. Nishio and co-workers proposed that the CH/π interaction be considered as the weakest kind of hydrogen bond, which is formed between a soft acid (CH) and a soft base (π−electrons).[8,9] In its weak limit, on the other hand, a hydrogen bond is hardly distinguished from van der Waals interactions (dispersion interaction and exchange repulsion).[2] With respect to the definition for hydrogen bonds, the CH/π interaction is considered to be located on the border between hydrogen bonds and van der Waals interactions.

In this paper, as the first step of a series of the cluster study on the CH/π interaction, we focus on the “activated” CH/π interaction found in clusters between aromatics and acetylene. Because of the relatively higher acidity of acetylenic CH (pK_a = 25) than those of alkane (pK_a = 49 for methane) and alkene (pK_a = 44 for ethylene),[14] the interaction between acetylenic CH and π-electrons is considered to be relatively stronger.[15] Such a stronger CH/π interaction is also expected for CH of haloforms,[16,17] and both of them are often called activated CH/π interaction.[9] Infrared (IR) spectroscopic studies of bulk solutions have demonstrated that low-frequency shifts of the CH stretching vibration of various substituted acetylenes occur upon association with aromatic molecules.[18] Similar frequency shifts were also found in a study of benzene−acetylene in the Ar matrix.[19] In NMR studies, a characteristic high field chemical shift was reported for the acetylenic proton with an increase of the concentration of the aromatic solvent, and it was interpreted in terms of the magnetic anisotropy of the aromatic ring, indicating the close contact between the acetylenic C−H bond and the aromatic π-electrons.[20,21] Though such bulk studies have demonstrated the presence of the CH/π interaction, detailed characterization of the nature of the interaction, such as favorable conformation between the acetylene molecule and the aromatic ring, and precise shifts of vibrational frequencies, has never been carried out because of the self-association and inhomogeneity of the bulk system.

Gas-phase cluster studies on the acetylenic CH/π interaction have been carried out mainly for benzene−acetylene clusters.[22−24] The S_1−S_0 electronic spectrum of benzene−acetylene was first reported by Carrasquillo et al.[22] They used mass-selected resonance-enhanced multiphoton ionization (REMPI), and attributed four bands to the $n = 1$ and 2 clusters of benzene−(acetylene)$_n$ involving their structural isomers. Later, Shelley et al. proposed a partial revision for the assignments of the cluster size on the basis of the acetylene concentration dependence and of the fluorescence lifetime measurements.[23] Sampson et al. finally provided firm conclusion of the cluster size assignments by using velocity- and mass-resolved REMPI spectroscopy.[24] All the cluster bands of benzene−acetylene appear at the high-frequency side of the corresponding transition of bare benzene, as seen in typical π-hydrogen-bonded clusters such as benzene−water.[25,26] High-level ab initio calculations on the benzene−acetylene cluster were carried out by Tsuzuki

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10.1021/jp049946b CCC: \$27.50

et al. and Novoa et al.[11,12] Both calculations predicted that acetylene locates on the C_6 axis of the benzene ring, and the electrostatic interaction is as important as the dispersion interaction in this system.

Very recently, Ramos et al. reported an infrared (IR) spectroscopic study of benzene−diacetylene (C_4H_2) clusters, investigating their CH stretching vibrations.[27] They found that the CH stretch frequency of the diacetylene moiety exhibits a characteristic low-frequency shift upon the cluster formation. With a help of theoretical calculations, π-bound structures, which are quite similar to those predicted for the benzene−acetylene clusters, were determined.

In the present study, we carry out IR spectroscopy for the CH stretching vibration of jet-cooled clusters of acetylene with various aromatics (benzene, toluene, *p*-xylene, mesitylene (1,3,5-trimethylbenzene), phenylsilane, ethylbenzene, naphthalene, and anthracene) in both the electronic ground (S_0) and first excited (S_1) states. Cluster structures are determined in combination with ab-initio calculations. Moreover, the intermolecular bond nature between acetylene and aromatic molecules is examined on the basis of the CH frequency shift of the acetylene moiety depending on the proton-accepting aromatics,.

II. Experiment

IR spectra of jet-cooled clusters were measured for S_0 and S_1 by using infrared−ultraviolet (IR−UV) and ultraviolet−infrared (UV−IR) double resonance techniques, respectively. Details of these techniques have been described elsewhere.[28] Briefly, in IR−UV spectroscopy for S_0, we monitor the fluorescence induced by a pulsed tunable UV laser, of which wavelength is fixed at the 0−0 or a particular vibronic band of the S_1-S_0 transition of a cluster. The fluorescence signal intensity is a measure of the population of the vibrational ground level in S_0. A tunable IR light pulse is introduced prior to the UV pulse by 50 ns. When the IR frequency is resonant on the vibrational transition of the cluster in S_0, a depletion of the fluorescence signal occurs as a result of the reduction of the population in the vibrational ground level. In UV−IR spectroscopy for S_1, on the other hand, the IR laser pulse is introduced just after the UV laser pulse. The vibrational transition in the S_1 state results in the reduction of the fluorescence intensity when the fluorescence quantum yield decreases upon the vibrational excitation. Thus, an IR spectrum is obtained as a depletion spectrum by monitoring the fluorescence intensity while scanning the IR frequency.

Aromatic samples (benzene, toluene, *p*-xylene, mesitylene, phenylsilane, ethylbenzene, naphthalene, and anthracene) were purchased from Tokyo Kasei Co. and Aldrich Co., and were used without further purification. The vapor of the aromatic sample was seeded in a helium/acetylene gaseous mixture of the stagnation pressure at 2−4 atm, and was expanded into a vacuum chamber. The acetylene concentration was 1−5%, and the vapor pressure of the aromatic samples was also controlled by the sample temperature to optimize the cluster signal intensity. The laser-induced fluorescence was detected by a photomultiplier tube (Hamamatsu 1P28) combined with color filters.

III. Results and Discussion

A. Electronic Spectra of X−(Acetylene)$_n$ Clusters. Fluorescence excitation spectra of X−(acetylene)$_n$ clusters (X = (a) benzene, (b) toluene, (c) *p*-xylene, (d) mesitylene, (e) phenylsilane, (f) ethylbenzene, (g) naphthalene, and (h) anthracene) are shown in Figure 1. In each spectrum, the UV laser wavelength was scanned around the 0−0 band of the S_1-S_0 transition of the aromatic molecular moiety, and new bands appearing with the addition of acetylene are attributed to clusters with acetylene. In the cases of benzene−acetylene and mesitylene−acetylene, the cluster transitions are probed at the 6^1_0 band region of the aromatic molecular moiety because their 0−0 bands are symmetry-forbidden in the bare molecules. The assignments of the cluster size (number of acetylene molecules in the cluster, *n*) were given on the basis of the number of the CH stretching vibration bands of the acetylene moiety observed in IR−UV spectroscopy, as described in detail later. In the anthracene−acetylene system, only cluster bands of $n = 2$ and 3 were found in the electronic spectrum (Figure 1h), and we could not find any band assigned to the cluster of $n = 1$.

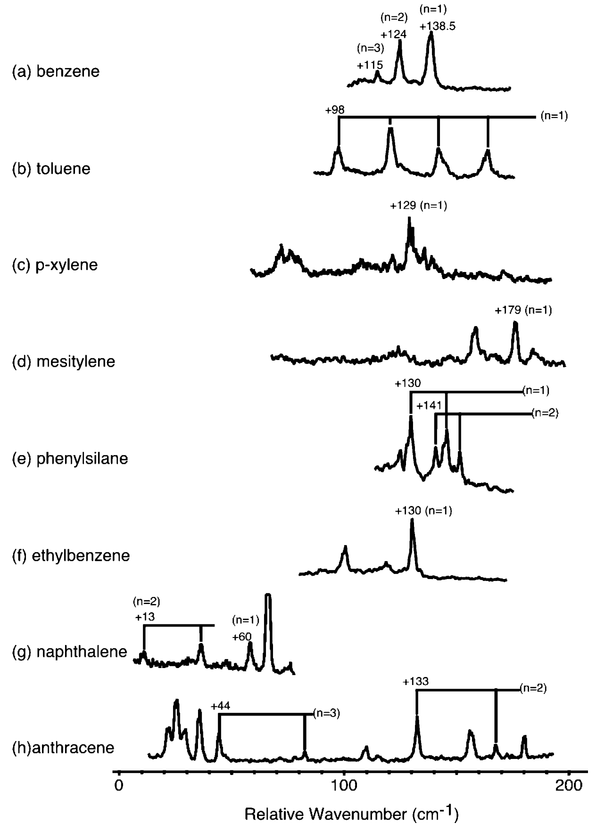


Figure 1. Fluorescence excitation spectra of X−(acetylene)$_n$ clusters (X = (a) benzene, (b) toluene, (c) *p*-xylene, (d) mesitylene, (e) phenylsilane, (f) ethylbenzene, (g) naphthalene, and (h) anthracene). The frequency is given relative to the 0−0 band of the S_1-S_0 transition of the associating monomer band of each aromatic moiety. Only in (a) and (d), the frequency is relative to the 6^1_0 band of each aromatic monomer. All the nonassigned bands are due to transitions of monomer molecules.

In π-hydrogen-bonded aromatic clusters, high-frequency shifts of the S_1-S_0 electronic transitions of the proton-accepting aromatic moiety are usually observed.[25,26] This is quite contrary to low-frequency shifts observed for aromatic van der Waals clusters.[29,30] In the spectra in Figure 1, all the cluster bands appear at the high-frequency side of the associating monomer band of the aromatic moiety. This fact suggests that the intermolecular bond between acetylene and aromatics has the π-hydrogen bond character.

The spectral features in the present spectrum of benzene−(acetylene)$_n$ (Figure 1a) are the same as those in the fluorescence excitation spectrum reported by Shelley et al.[23] The firm assignments of the cluster size were already given by Sampson et al.,[24] and IR−UV spectroscopy in the present study supports

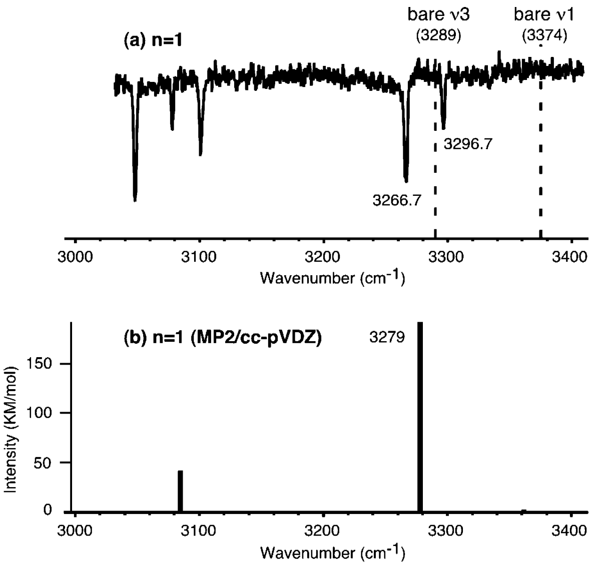


Figure 2. (a) IR spectrum of benzene−acetylene in S_0. Deperturbed vibrational frequencies of CH stretching vibrations in bare acetylene are indicated by the dashed lines. (b) Simulated IR spectrum of benzene−acetylene at the MP2/cc-pVDZ calculations. The frequencies were calculated on the basis of the stable structure, which is schematically seen in Figure 4(b), and were scaled by the scaling factor of 0.9526.

their assignments, as described later. It was reported by Carrasquillo et al. and by Shelley et al. that the cluster band associated with the 0−0 band of the benzene moiety is still forbidden for $n = 1$, but is allowed for $n = 2$ and 3.[22,23] This means that the $n = 1$ cluster holds the C_6 symmetry axis, while the symmetry of the cluster is lower than C_3 in the $n = 2$ and 3 clusters.

B. Infrared Spectra in S_0. *(a) IR Spectra of Bare Acetylene and Its Homo Dimer.* Prior to presenting IR spectra of the X−(acetylene)$_n$ clusters, here we briefly summarize the characteristics of the CH stretching vibrations of bare acetylene and its homo dimer, which have been extensively studied so far.[31−33] In bare acetylene, the anti-symmetric CH stretching vibration (ν_3) is IR-active while the symmetric CH stretching vibration (ν_1) is IR inactive because of the symmetry. The ν_3 mode is subject to an extensive Fermi mixing with the combination of $\nu_2+\nu'_4+\nu'_5$, and the perturbed vibrational frequencies are 3294.9 and 3281.9 cm^{-1}. The deperturbed frequencies were evaluated to be 3288.7 cm^{-1} for ν_3 and 3288.1 cm^{-1} for $\nu_2+\nu'_4+\nu'_5$. The vibrational frequency of the ν_1 mode is 3374 cm^{-1}.

The acetylene homo dimer has a T-shape structure, where the π-electrons of one acetylene moiety accept the proton of the other moiety.[32,33] In the proton-donating acetylene moiety, the two CH bonds are no longer equivalent. In both the acetylene moieties, however, the ν_1 vibration is still IR inactive because of the small magnitude of the perturbation. On the other hand, the Fermi mixing between ν_3 and $\nu_2+\nu'_4+\nu'_5$ would be lifted so that the combination band is no longer observed in the IR spectra of the acetylene dimer. The ν_3 frequencies were reported to be 3273 and 3281 cm^{-1} for the proton-donating and -accepting moieties, respectively.

(b) IR spectrum of Benzene-(Acetylene)$_n$: Direct Evidence for the Activated CH/π Interaction. Because benzene−(acetylene)$_n$ is the prototype of all the X−(acetylene)$_n$ clusters in this study, we describe their IR spectra in detail. Figures 2a and 3a show the IR−UV spectra of the $n = 1$ and $n = 2$ clusters of benzene−(acetylene)$_n$ in S_0, respectively. These spectra were measured by tuning the UV frequency at the +138.5 and +124 cm^{-1} bands in the fluorescence excitation spectrum (Figure 1a), respectively, while the IR wavelength was scanned in the 3 μm region. In both IR spectra, two band groups are seen in 3000−3100 and 3250−3300 cm^{-1}. The former group is attributed to the CH stretching vibrations of the benzene moiety, and the latter is to the acetylenic CH stretching vibrations.

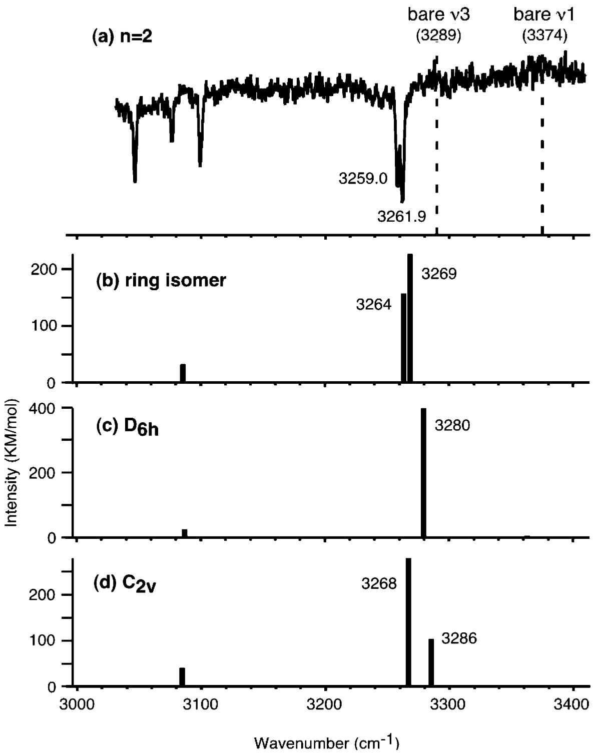
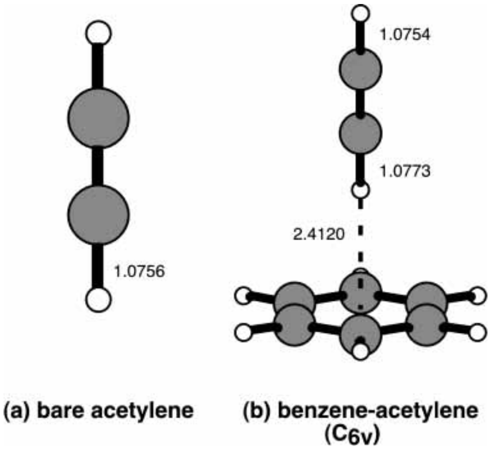


Figure 3. (a) IR spectrum of benzene−(acetylene)$_2$ in S_0. (b)−(d) Simulated IR spectra of benzene−(acetylene)$_2$ at MP2/cc-pVDZ. The calculated frequencies were based on the (b) ring, (c) D_{6h}, and (d) C_{2v} stable structures, respectively, which are schematically shown in Figure 5. The scaling factor of 0.9526 was applied to the calculated frequencies.

In the spectrum of the $n = 1$ cluster, the strong band appearing at 3266.7 cm^{-1} is readily assigned to the ν_3 band of the acetylene moiety. The ν_3 band shows a remarkable low-frequency shift of 22 cm^{-1} from the deperturbed frequency of the bare molecule. On the other hand, the CH stretching bands of the benzene moiety are hardly perturbed by the cluster formation; no significant shift (within 1 cm^{-1}) is seen for the three bands resulting from the Fermi mixing between the IR-active CH stretch mode ν_{20} and three combination bands, and their relative intensities are also very similar to those of bare benzene.[34] Such a spectral feature of the cluster clearly demonstrates that the intermolecular bond between acetylene and benzene is of a π-hydrogen-bond type, where acetylene donates its proton to π-electrons of benzene.

The harmonic frequencies of the $n = 1$ cluster, which can be compared with the present result, were unfortunately not given in the previous high-level ab initio calculations by Tsuzuki et al. (at MP2/cc-pVQZ) and Novoa et al. (at MP2/6-31+G(2d,-2p)).[11,12] Thus, we carried out ab-initio calculations at the MP2/cc-pVDZ level for the stable cluster structure of the C_{6v} symmetry by using the Gaussian 98 program package,[35] and evaluated its harmonic frequencies. The calculated stable structure is shown in Figure 4b in comparison with the calculated structure of bare acetylene (Figure 4a).[36] The simulated IR spectrum based on this cluster structure is displayed in Figure 2b in comparison with the observed spectrum (Figure 2a). The calculated harmonic frequencies were scaled by the factor of 0.9526, which is determined to reproduce the ν_1 and deperturbed



(a) bare acetylene (b) benzene-acetylene (C_{6v})

Figure 4. Schematic ab-initio structures of (a) bare acetylene and (b) benzene–acetylene at MP2/cc-pVDZ. Values in the figures show the bond distances in angstroms.

ν_3 vibrational frequencies of bare acetylene at the same calculation level. In our calculations, the binding energy of the cluster was evaluated to be 2.602 kcal/mol, including the zero-point energy (ZPE) and basis set superposition error (BSSE) corrections. The BSSE correction was made by the functional counterpoise method.[37] This calculated binding energy covers 77% of that of the MP2 calculations at the basis set limit (3.36 kcal/mol), which was evaluated by Tsuzuki et al. [11] Even at this level of calculations, the calculated ν_3 frequency of the cluster shows the low-frequency shift of 10 cm^{-1} from the deperturbed ν_3 frequency of the bare molecule, and it qualitatively reproduces the observed spectral feature.

The observed low-frequency shift of 22 cm^{-1} for the acetylenic ν_3 band in benzene–acetylene is much larger than the shift of 16 cm^{-1} found for the proton-donating site of the T-shaped acetylene dimer.[32,33] The difference between the proton affinities of benzene and acetylene (179.3 and 153.3 kcal/mol, respectively) might be reflected in the difference of the frequency shifts.[38] A recent IR study in the Ar matrix also reported a similar low-frequency shift of the ν_3 vibration of acetylene due to the cluster formation with benzene.[19] In this case, however, the frequency shift is only 13 or 16 cm^{-1} depending on the site inhomogeneity, and is much smaller than that observed in the present gas-phase cluster study. The difference of the frequency shift suggests that interaction between acetylene and benzene is strongly perturbed by the surrounding Ar atoms, and the binary cluster picture is not a good approximation in the Ar matrix.

The ν_1 band of the acetylene moiety is not seen in the IR spectrum of the $n = 1$ cluster, though the shift of the ν_3 band indicates that the two CH oscillators are no longer equivalent in the cluster. The absence of the ν_1 band was also reported for the T-shaped acetylene dimer.[32,33] These facts suggest that the normal mode picture is still held in the acetylene moiety of the cluster because of the small magnitude of the perturbation. The MP2/cc-pVDZ calculations also support the negligible symmetry breakdown in the vibrational structure of the acetylene moiety. The ν_1 frequency is predicted to be 3363 cm^{-1} (after scaling) in the C_{6v} cluster, and the calculated oscillator strength of the ν_1 band is only 1.5% of that of the ν_3 band. These calculation results are consistent with the disappearance of the ν_1 band in the observed IR spectrum.

In the closely analogous system, benzene–diacetylene, a similar C_{6v} structure was determined by Ramos et al. on the basis of IR spectroscopy of the jet-cooled cluster.[27] The IR spectrum of benzene–diacetylene is quite similar to that of benzene–acetylene. The acetylenic CH frequency shift is, however, much larger (about 40 cm^{-1}) and the symmetric CH stretch band clearly appears in the IR spectrum. These features indicate the relatively stronger intermolecular interaction in benzene–diacetylene. Moreover, the π-bound CH stretch of the diacetylene moiety split into two bands having almost even intensities, and it is attributed to the Fermi mixing with a combination band.

Also in benzene–acetylene, a weak band is seen near the acetylenic CH band (+30 cm^{-1}). This band at 3296.7 cm^{-1} would be attributed to the combination of $\nu_2+\nu'_4+\nu'_5$ associating with the strong Fermi mixing with ν_3 in bare acetylene[31] or the combination of the acetylenic CH and an intermolecular mode. The former case seems to be less probable because (i) no correspondent band appears in the spectrum of the $n = 2$ cluster despite the similar low-frequency shifts of ν_3 to that in the $n = 1$, as described later, and (ii) the combination of $\nu_2+\nu'_4+\nu'_5$ is also absent in IR spectra of the T-shaped acetylene homo dimer, though the homo dimer exhibits the even smaller shift of the acetylenic CH stretching vibration.[32,33] The MP2/cc-pVDZ level calculations for the C_{6v} cluster structure predicted an intermolecular bending mode which has a vibrational frequency of 39 cm^{-1}. This bending mode would contribute to the combination band though this assignment is still tentative.

The IR spectrum of the $n = 2$ cluster is similar to that of $n = 1$, but two ν_3 bands of acetylenic CH stretching vibrations are seen at 3259.0 and 3261.9 cm^{-1}. The appearance of these two ν_3 bands supports the assignment of the cluster size given in the previous studies on the electronic spectra.[22–24] Similar to the $n = 1$ cluster, the ν_1 band is absent. On the other hand, the combination band near the ν_3 band disappears in the $n = 2$ cluster. Both of the ν_3 bands show low-frequency shifts, indicating that both the acetylene molecules are donating their proton in the cluster.

We carried out ab-initio calculations also for the $n = 2$ cluster at the MP2/cc-pVDZ level. Three stable structures, ring, D_{6h}, and C_{2v}, were found, and their schematic structures are reproduced in Figure 5 a, c, and d, respectively. When we assume the acetylene dimer subunit of the C_{2h} symmetry, the dimer subunit cannot hold its symmetry in the energy optimization procedure at this level of calculations, and such an initial structure finally results in the stable ring structure or is trapped at the transient zigzag structure shown in Figure 5b. The D_{6h} structure was the global energy minimum at this level of calculation (its binding energy was estimated to be 5.063 kcal/mol, including the ZPE and BSSE corrections), though the energy difference from the ring structure is almost negligible (+0.106 kcal/mol). The C_{2v} structure is estimated to be slightly less stable (+1.517 kcal/mol). The IR spectra were also simulated on the basis of these ab-initio stable structures. The simulated IR spectra are shown in Figure 3b–d in comparison with the observed spectrum (spectrum a). Though the D_{6h} structure is the global minimum at this level of calculation, a single antisymmetric CH band is expected to appear in its IR spectrum. Therefore, we safely rule out this structure. The ring structure is estimated to be more stable than the C_{2v} structure in energy. Moreover, only the ring structure well reproduces the observed IR feature. Thus, we conclude the ring structure is the most probable for the $n = 2$ cluster. This is consistent with the indication from the electronic spectroscopic studies that the 0–0 band of the S_1-S_0 transition is no longer forbidden in $n = 2$, representing the cluster symmetry lower than C_3. [22, 23]

This ring-type structure bound by three CH/π hydrogen bonds was first predicted in ab-initio calculations by Sundararajan et

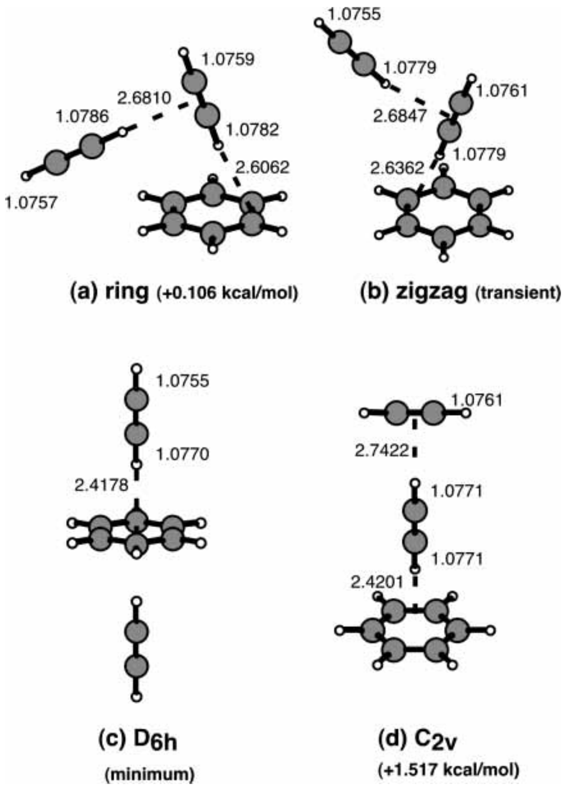


Figure 5. Schematic ab-initio structures of benzene−(acetylene)$_2$ for (a) ring, (b) zigzag, (c) D_{6h}, and (d) C_{2v} isomers at MP2/cc-pVDZ. The relative energies including the ZPE and BSSE corrections are shown in parentheses. The zigzag isomer is a transient in this calculation. Values in the figures show the bond distances in angstroms.

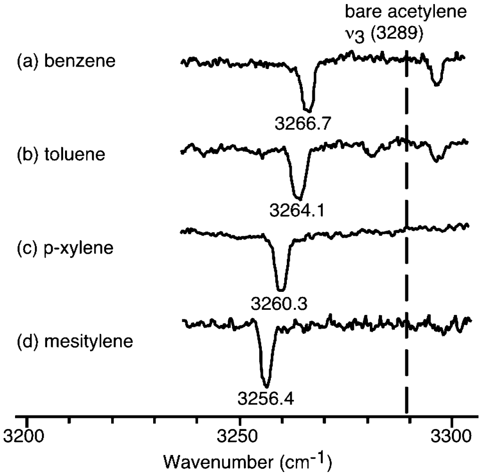


Figure 6. Acetylenic ν_3 vibrational region in IR spectra of the X−(acetylene)$_1$ clusters (X = (a) benzene, (b) toluene, (c) *p*-xylene, and (d) mesitylene) in S_0.

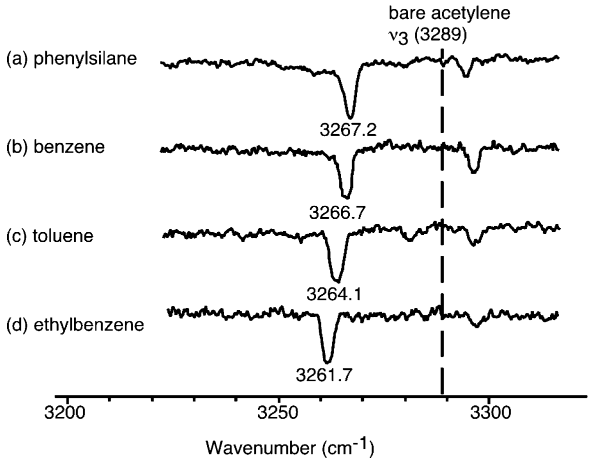


Figure 7. Acetylenic ν_3 vibrational region in IR spectra of X−(acetylene)$_1$ clusters (X = (a) phenylsilane, (b) benzene, (c) toluene, and (d) ethylbenzene) in S_0.

al., though no IR absorption band attributed to the $n = 2$ cluster was found in their Ar matrix experiment.[19] A similar ring structure was also suggested for the analogous cluster, benzene−(diacetylene)$_2$, by Ramos et al.[27] In their study, however, the structural determination was less firm because of the overlap of bands due to higher cluster in the observed IR spectrum. The present results for benzene−(acetylene)$_2$ strongly support the previous structural determination for benzene−(diacetylene)$_2$.

Though a weak band due to the $n = 3$ cluster is seen in the electronic spectrum (Figure 1 a), the IR spectrum of the $n = 3$ cluster could not be measured in the present study because of the interference of the background signal due to higher clusters.

(c) IR Spectra of Substituted Benzene−Acetylene Clusters: π-Electron Density Dependence of the Activated CH/π Interaction. To examine the nature of the intermolecular interaction between the acetylenic CH and the aromatic ring in detail, we observed shifts of the ν_3 vibrational frequency in the various substituted benzene−acetylene binary clusters. Shown in Figure 6 is the acetylenic ν_3 vibrational region in IR spectra of the X−(acetylene)$_1$ clusters (X = (a) benzene, (b) toluene, (c) *p*-xylene, and (d) mesitylene) in S_0. The methyl group is a weak electron-donating group to the aromatic ring, and it is reasonably expected to increase the π-electron density with increase of the number of the methyl groups substituted to the ring. Figure 6 shows that the magnitude of the low-frequency shift of the ν_3 band increases with the number of the methyl groups. This is a clear demonstration of the π-hydrogen-bond nature of the activated CH/π interaction.

Such a dependence of the acetylenic ν_3 frequency upon the π-electron density is also observed when the substituent of a different type is introduced instead of the increase of the number of the methyl groups. Figure 7 shows IR spectra of X−(acetylene)$_1$ clusters (X = (a) phenylsilane, (b) benzene, (c) toluene, and (d) ethylbenzene) in S_0. The substitution of an electron-donating group such as methyl or ethyl groups enhances the low-frequency shift of the ν_3 band in comparison with that in benzene−acetylene. On the other hand, the silyl substitution reduces the low-frequency shift. The silyl group is known to be π-electron attracting,[39] and the high-frequency shift can be regarded as an indication of the reduction of the π-hydrogen-bond strength.

In an ordinary hydrogen bond, it is well-known that the attractive force is composed of many contributions including electrostatic interactions.[1−4] With a decrease of the hydrogen bond strength, however, the contribution of the dispersion interaction becomes relatively important as an attractive component among the intermolecular interactions, and such a weak hydrogen bond would finally converge into the van der Waals interaction at its weak limit. The CH/π interaction is considered to locate in a gray zone lying between the ordinary hydrogen bond and the van der Waals interaction. For the activated CH/π interaction in benzene−acetylene, the previous ab-initio study by Tsuzuki et al. predicted that the contribution of the dispersion interaction is as important as the electrostatic interaction.[11] To experimentally probe the role of the dispersion interaction in the activated CH/π interaction, we examined the correlation between the shift of the acetylenic ν_3 band and the polarizability

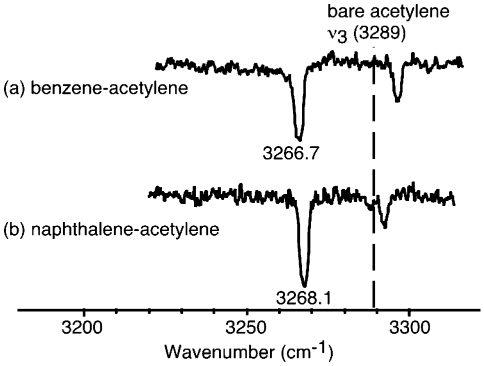


Figure 8. Comparison between the acetylenic ν_3 vibrational region of IR spectra of (a) benzene−acetylene and (b) naphthalene−acetylene in S_0.

of the proton-accepting aromatics. Figure 8 is the comparison between the IR spectra of (a) benzene−acetylene and (b) naphthalene−acetylene in S_0. With an increase of the number of the aromatic ring, the averaged polarizability remarkably increases, $\alpha = 10.3 \times 10^{-24}$ and 16.5×10^{-24} Å^3 for benzene and naphthalene, respectively.[40] Here, we refer to the magnitude of the mean values of the anisotropic polarizabilities as a measure of the dispersion interaction. Despite the increase of the polarizability, the cluster formation with naphthalene causes the slightly smaller low-frequency shift of the acetylenic ν_3 band than that with benzene.

A similar trend, that is, a negative correlation between the polarizability and the magnitude of the low-frequency shift is also found in the $n = 2$ clusters. Shown in Figure 9 are IR spectra of (a) benzene−(acetylene)$_2$, (b) naphthalene−(acetylene)$_2$, and (c) anthracene−(acetylene)$_2$ in S_0. For the anthracene−acetylene system, the minimum cluster size we found was $n = 2$, as described in section III.A. In each spectrum, two acetylenic ν_3 bands appear, supporting the assignment of the cluster size. Moreover, the similarity among these three IR spectra indicates that all of the clusters should have essentially the same ring structure as suggested for benzene−acetylene in section III.B.b. The IR spectra of the clusters of $n = 2$ also show that the low-frequency shifts of both the ν_3 bands of the cluster with anthracene are less than those of the clusters with benzene or naphthalene, though the polarizability of anthracene is known to be $\alpha = 25.4 \times 10^{-24}$ Å^3, which is much larger than that of benzene or naphthalene. [40]

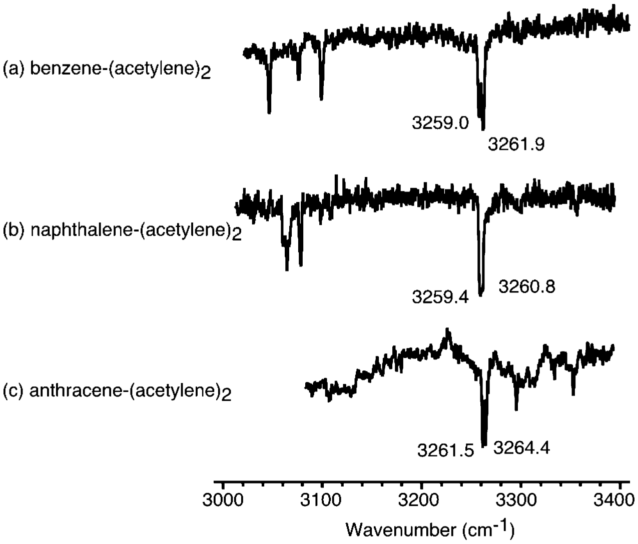


Figure 9. IR spectra of (a) benzene−(acetylene)$_2$, (b) naphthalene−(acetylene)$_2$, and (c) anthracene−(acetylene)$_2$ in S_0.

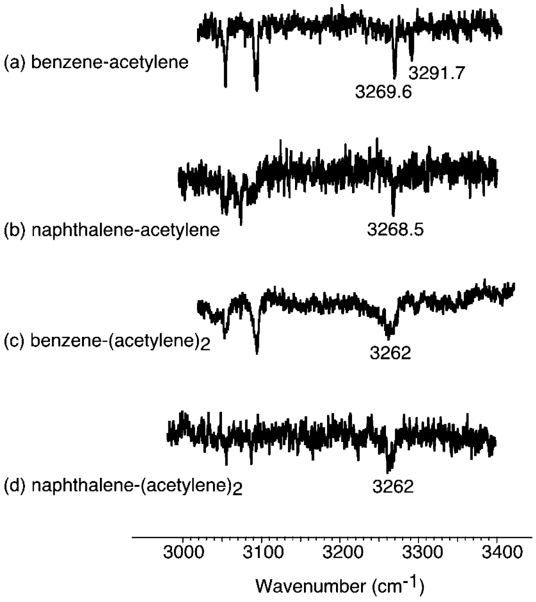


Figure 10. IR spectra of (a) benzene−acetylene, (b) naphthalene−acetylene, (c) benzene−(acetylene)$_2$, and (d) naphthalene−(acetylene)$_2$ in S_1.

These results demonstrate that the activated CH/π interaction strength exhibits a negative correlation with the averaged polarizability. In aromatic molecule−Ar van der Waals clusters, on the other hand, the binding energy of the cluster actually increases with the number of the aromatic ring, and the increase of the binding energy in each step is especially remarkable (20−30%) in the first two steps (from one ring to three rings).[41] Such a feature of the van der Waals clusters is quite contrary to the present aromatic−acetylene system, suggesting that the dispersion interaction is less important in the activated CH/π interaction. With respect to this point, it is clear that the activated CH/π interaction should be categorized to the π-hydrogen bond rather than the van der Waals interaction. Though the averaged polarizability increases with the number of the aromatic rings in the molecule, the π-electron density slightly decreases because of sharing π-electrons among the rings. The π-electron number per ring is $6/1 = 6$, $10/2 = 5$, and $14/3 = 4.7$ for benzene, naphthalene, and anthracene, respectively. The observed negative correlation between the aromatic ring number and the ν_3 frequency shift would reflect the local π-electron density around the donated proton rather than the polarizability of the acceptor molecule.

C. Infrared Spectra in S_1. Electronic excitation effects on the CH/π interaction are also studied with IR spectroscopy of the clusters in the S_1 state. Figure 10 shows the IR spectra of (a) benzene−acetylene, (b) naphthalene−acetylene, (c) benzene−(acetylene)$_2$, and (d) naphthalene−(acetylene)$_2$ in S_1. In each cluster, the acetylenic ν_3 band is high-frequency shifted in comparison with that in S_0, representing the reduction of the CH/π interaction strength upon the electronic excitation. This is consistent with the high-frequency shift of the electronic transition associated with the cluster formation, as seen in section III.A. The acetylenic ν_3 frequency shift upon the electronic excitation is 2.9 and 0.4 cm^{-1} in benzene−acetylene and naphthalene−acetylene, respectively. Therefore, different from the case in S_0, the ν_3 frequency in S_1 is rather higher in benzene−acetylene than in naphthalene−acetylene. This is also consistent with the smaller high-frequency shift of the electronic transition in naphthalene−acetylene (60 cm^{-1}) than benzene−acetylene (139 cm^{-1}). A π-hydrogen bond is generally weakened upon the electronic excitation of the proton-accepting aromatic site, while the dispersion interaction is enhanced.[25,26,29,30,41] In naphthalene−acetylene, both the electronic and IR spectra show that the weakening of the π-hydrogen bond strength is less remarkable than benzene−acetylene, and this might be attributed to the relatively larger contribution of the dispersion interaction in naphthalene−acetylene. Also in the $n = 2$ clusters, the small decrease of the ν_3 frequency shifts is seen upon the photoexcitation, though the bands are broaden in S_1 and the precise estimation of the band shifts is difficult.

IV. Concluding Remarks

In this study, we applied IR spectroscopy to jet-cooled clusters of acetylene with various aromatic molecules to characterize the microscopic nature of the interaction between the acetylenic C−H bond and aromatic rings. The acetylenic CH stretching vibrations of the clusters were observed in S_0 and S_1. Upon the cluster formation, the acetylenic CH stretch band showed a distinct low-frequency shift which is the consequence of the activated CH/π interaction in these clusters. The magnitude of the low-frequency shifts clearly depended on the π-electron density of the proton-accepting aromatic molecules, while only a negative correlation was seen against the polarizability of the aromatics. The electronic excitation of the aromatic ring moiety slightly decreased the frequency shifts. No high-frequency shift of the acetylenic CH stretch was found for any clusters in the present study. The acidity of the acetylenic CH bond is much higher than those of the alkyl CH bonds, and the present results indicated that the intermolecular interaction between the activated CH group and the π-electrons is clearly categorized to the conventional π-hydrogen bond rather than the van der Waals interaction.

This study demonstrated the validity of IR spectroscopy of isolated molecular clusters in the gas phase to probe the microscopic nature of weak intermolecular interactions. The typical CH/π interaction due to the alkyl CH bond would be much closer to the border between π-hydrogen bonds and van der Waals interactions. As a series of the cluster study on the CH/π interaction, IR spectroscopy of aromatics−methane clusters is now going on in our laboratory.

Acknowledgment. The authors thank Dr. H. Ishikawa and Dr. T. Maeyama for their helpful discussion. This work was partly supported by the Grant-in-Aids for Scientific Research (14540462) by the Ministry of Education, Science, Sports, and Culture, Japan.

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