Structure of the Phenylacetylene−Water Complex as Revealed by Infrared-Ultraviolet Double Resonance Spectroscopy

Prashant Chandra Singh, Biswajit Bandyopadhyay, and G. Naresh Patwari*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076 India

Received: October 25, 2007; In Final Form: January 14, 2008

The structure of the phenylacetylene−water complex has been elucidated based on spectral shifts in electronic and vibrational transitions. Phenylacetylene forms a cyclic complex with water incorporating C−H···O and O−H···π hydrogen bonds, which is different from both the benzene−water and acetylene−water complexes, even though phenylacetylene combines the features of both benzene and acetylene. Formation of such a complex can be rationalized on the basis of cooperativity between the two sets of hydrogen bonds.

Introduction

It is now well-established that water interacts with the π electron density of the benzene ring resulting in formation of O−H···π hydrogen bond,[1] whereas the acetylene−water complex is characterized by a linear C−H···O hydrogen bond.[2] This implies that the role of water is reversed from donor to acceptor when the hydrogen-bonding partner is switched from benzene to acetylene. In the light of these observations, an interesting question arose: How would water interact with phenylacetylene, which incorporates features of both benzene and acetylene. In other words, the question that we address is whether water prefers to be a donor (similar to benzene−water) or an acceptor (similar to acetylene−water) when made to interact with phenylacetylene. We report here the vibrational spectroscopic evidence for determination of the structure of the phenylacetylene−water complex using IR-UV double-resonance spectroscopy.[3]

Experiment

The details of the experimental setup have been described elsewhere.[4] Briefly, helium buffer gas at 4 atm is bubbled through a mixture of phenylacetylene (Aldrich) and water kept at room temperature and expanded through a 0.5 mm diameter pulsed nozzle (Series 9, Iota One; General Valve Corporation). The electronic excitation of phenylacetylene and its water cluster was achieved using a frequency-doubled output of a tunable dye laser (Narrow Scan GR; Radiant Dyes; Coumarin-540A dye) pumped with third harmonic of a Nd:YAG laser (Surelite I-10; Continuum). The fluorescence excitation spectra were recorded by monitoring the total fluorescence with a photomultiplier tube (9780SB+1252-5F; Electron Tubes Limited) and a filter (WG-320) combination, while scanning the UV laser frequency. The IR spectra were obtained using the fluorescence dip infrared (FDIR) spectroscopic method. In this method, the population of a target species is monitored by fluorescence intensity following its electronic excitation to the $S_1 \leftarrow S_0$ origin band with a UV laser pulse. A tunable IR laser pulse is introduced 100 ns prior to the UV laser pulse. When the IR frequency is resonant with the vibrational transition of the target species, the ground-state population decreases, resulting in the depletion of the fluorescence signal. In our experiments the source of tunable IR light is an idler component of a $LiNbO_3$ OPO (Custom IR OPO; Euroscan Instruments) pumped with an injection-seeded Nd:YAG laser (Briliant-B; Quantel).[5] The typical energies used were about 100 μJ/pulse for the UV laser and about 2 mJ/pulse for the IR laser and the bandwidth of both the UV and IR lasers is about 1 cm^{-1}. Typically 50% depletion was observed for C−H stretching vibration of phenylacetylene, while 80−90% depletion was observed for both C−H and O−H vibrations of the complex.

Results and Discussion

Figure 1A shows the fluorescence excitation spectrum of phenylacetylene, and the intense peak at 35 876 cm^{-1}, marked with asterisk, corresponds to band origin of the $S_1 \leftarrow S_0$ transition, which is in good agreement with the value reported in the literature.[6] Figure 1B shows the fluorescence excitation spectrum in the presence of water and the transition at 35 890 cm^{-1}, marked with "+" is due to the complex. This transition is present even without addition of water, presumably due to residual water in the gas lines; however, it gains intensity upon addition of water. The band origin of phenylacetylene−water complex is shifted by 14 cm^{-1} to the blue, relative to bare phenylacetylene, consistent with the reported value.[6b] Comparison with the benzene−water complex, for which the $6a_0^1$ electronic transition is shifted to the blue by 50 cm^{-1},[1d] suggests that, unlike the benzene−water complex, the water may be not be interacting with the π electron density of benzene ring in phenylacetylene.

The FDIR spectra of phenylacetylene and phenylacetylene−water were recorded by monitoring the fluorescence following excitation at their corresponding band origin transitions at 35 876 and 35 890 cm^{-1}, respectively, and scanning the IR laser frequency. Figure 2A depicts the FDIR spectrum of bare phenylacetylene, which shows several transitions. Sterns and Zwier have assigned the two strong transitions at 3325 and 3343 cm^{-1} to the Fermi resonance bands between the C−H stretching vibration and a combination of one quantum of C≡C stretch and two quanta of C≡C−H out-of-plane bend and other weak features to the transitions arising out of higher order coupling terms.[7] Surprisingly, the FDIR spectrum of phenylacetylene−water, depicted in Figure 2B, has a single transition at 3331 cm^{-1}. From this spectrum one can infer that addition of a water

---

* To whom correspondence should be addressed. E-mail: naresh@chem.iitb.ac.in.

10.1021/jp710311p CCC: $40.75

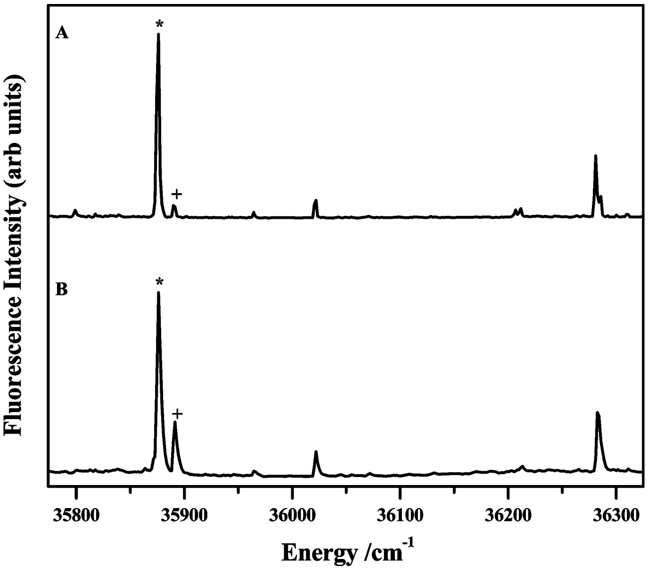

Figure 1. Fluorescence excitation spectrum of (A) phenylacetylene and (B) phenylacetylene in the presence of water. In both the traces the peaks marked with "*" and "+" are band-origin transitions for phenylacetylene and phenylacetylene−water, respectively.

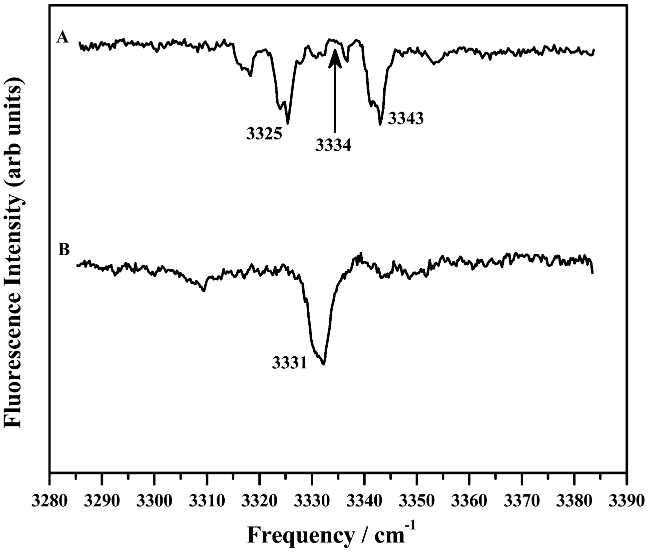

Figure 2. FDIR spectrum of (A) phenylacetylene and (B) phenylacetylene−water in the acetylenic C−H stretching region. In part A, the arrow indicates the position of unperturbed C−H oscillator.

molecule perturbs the Fermi resonance condition, leading to a single transition, which can be assigned to the acetylenic C−H stretching vibration of the complex. The FDIR spectrum of phenylacetylene−water complex in the O−H stretching region is presented in Figure 3. This spectrum consists of a sharp transition at 3724 cm^{-1} and relatively broad band at 3629 cm^{-1}. In several hydrogen-bonded complexes involving water as the hydrogen-bond donor, the free O−H stretching vibration is known to occur around 3725 cm^{-1} and the hydrogen-bonded O−H stretching to a further lower frequency depending upon the strength of the hydrogen bond.[8] Comparison with the present case leads to a straightforward assignment of the sharp transition at 3724 cm^{-1} and relatively broad band at 3629 cm^{-1} to free and hydrogen-bonded O−H stretching vibrations of water molecule, respectively.

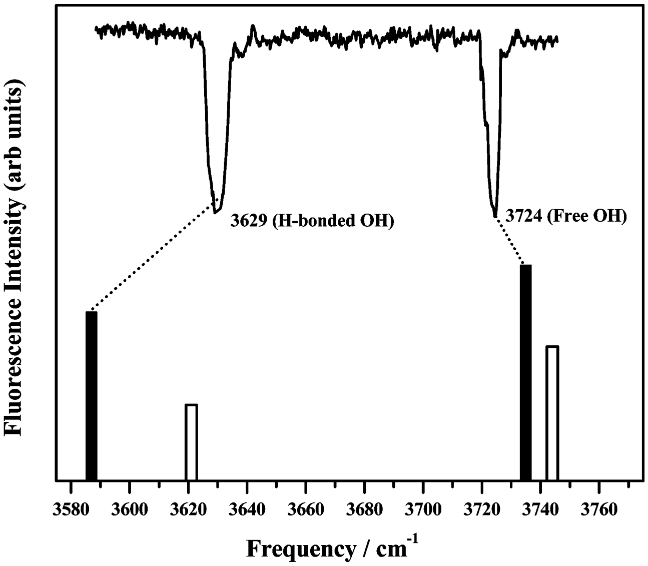

Figure 3. FDIR spectrum of phenylacetylene−water in the O−H stretching region. Also shown are the calculated vibrational (stick) spectra for the complexes B (open bars) and C (solid bars) for comparison.

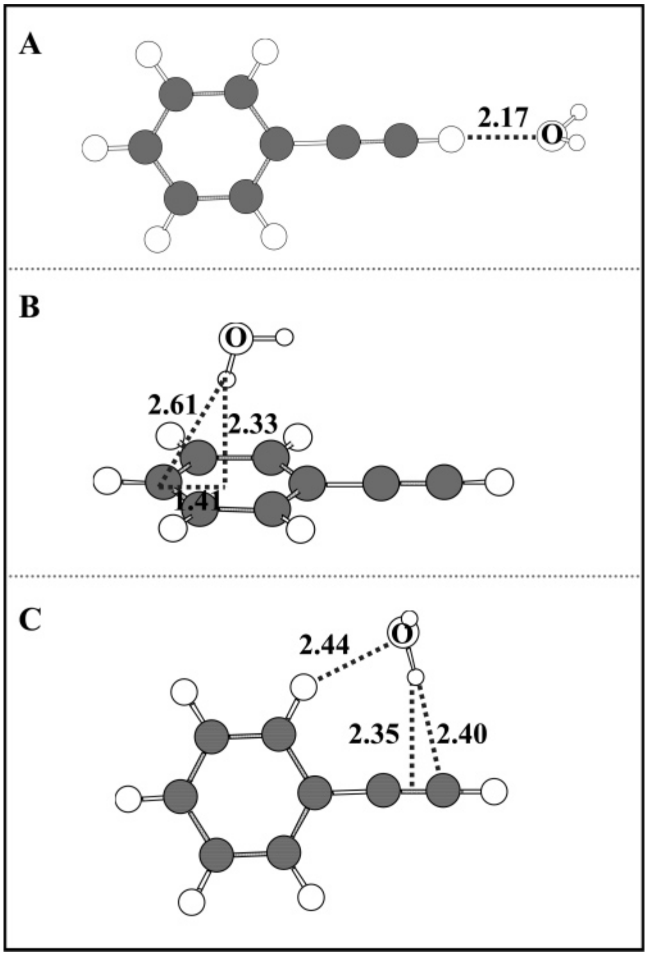

Figure 4. Calculated structures of phenylacetylene−water complexes at the MP2/aug-cc-pVDZ level. Distances are shown in angstroms.

To elucidate the structure of phenylacetylene−water complex we carried out ab initio calculations at MP2/aug-cc-pVDZ level of theory using Gaussian 98.[9] These calculations converge on to three different minima, structures of which are shown in Figure 4. The first structure (A; Figure 4) is a C−H···O "σ" hydrogen-bonded complex with phenylacetylene acting as a hydrogen bond donor to the water molecule, a structure similar to the acetylene−water complex.[2] The second structure (B; Figure 4) is a O−H···π hydrogen-bonded complex, wherein

TABLE 1: Binding Energies (kJ mol^{-1}) and Scaled Vibrational Frequencies (cm^{-1}) and Their Shifts for the Three Phenylacetylene−Water Complexes Calculated at the MP2/aug-cc-PVDZ Level of Theory[a]

	ΔE	ν_{C-H}	$\Delta\nu_{C-H}$	ν_{O-H} (s, as)	$\Delta\nu_{O-H}$
PHA		3335			
water				3644 (s), 3772 (as)	
A	8.7	3274	−61	3641 (s), 3769 (as)	−3, −3
B	11.2	3333	−2	3621 (hb), 3744 (f)	−23, −28
C	11.3	3328	−7	3587 (hb), 3735 (f)	−57, −37

[a] For the O−H vibrations "s", "as", "hb", and "f" indicate symmetric, antisymmetric, hydrogen-bonded, and free stretching frequencies, respectively.

the benzene ring of the phenylacetylene moiety acts as hydrogen bond acceptor, similar to the benzene−water complex.[1] Interestingly, the calculations also yield a third structure (C; Figure 4) in which both the phenylacetylene and water molecules act as donor and acceptor leading the formation of a quasiplanar cyclic complex. In this case the O−H of water molecule is hydrogen bonded to the π electron density of acetylenic C≡C triple bond and the C−H group of benzene ring in the ortho position is hydrogen bonded to oxygen of the water moiety. Table 1 lists the zero point vibrational energy (ZPVE) and basis set superposition error (BSSE) corrected binding energies. According to Kim et al., 100% of BSSE correction often underestimates the interaction energy, and 50% correction is a good empirical approximation.[10] Therefore we report binding energies with 50% BSSE correction. Though it is conceived that the acetylenic O−H is fairly acidic in phenylacetylene, the C−H···O "σ" hydrogen-bonded complex (**A**) is least stable. On the other hand both the O−H···π (B) and the cyclic (C) hydrogen-bonded complexes have almost identical binding energies.

It has been long realized that the IR spectroscopy of X−H stretching vibrations, such as O−H, N−H, and even C−H groups, is an important spectroscopic tool for the identification of hydrogen bonding.[11] This is due to the fact that these groups being involved directly are very sensitive to hydrogen-bonded structures, and show a characteristic shift to a lower frequency upon hydrogen bonding. On the basis of the shifts in the vibrational transitions one can assign the possible intermolecular structure of the complex. The calculated and scaled vibrational frequencies of the two monomers (phenylacetylene and water) and the three complexes at MP2/aug-cc-pVDZ level are also listed in Table 1, along with the frequency shifts. The scaling factor of 0.958 was chosen so as to match the experimental vibrational frequencies of the monomers and the same scaling factor was used for the complexes. For the σ hydrogen-bonded complex (A) the acetylenic C−H stretching vibration shows a substantial shift of 61 cm^{-1} to a lower frequency. On the other hand for the π hydrogen-bonded (B) and cyclic (C) complexes the corresponding shift is marginal. From Figure 2 the frequency corresponding to the unperturbed acetylenic C−H group can be estimated as 3334 cm^{-1},[12,13] which implies that the shift in the acetylenic C−H stretching vibration of phenylacetylene upon interaction with water is −3 cm^{-1}. On the basis of very small shift in the acetylenic C−H stretching vibration the "σ" hydrogen-bonded complex (A) can be ruled out as the possible structure.

Figure 3 also shows the comparison between the experimental and calculated (stick) vibrational spectrum in the O−H stretching region. It appears that the vibrational frequencies of the π hydrogen-bonded complex (B) and the intensities of the cyclic complex (C) are in agreement with the experimental spectrum. The calculations predict that the O−H stretching frequencies of the water moiety in complexes B and C are red-shifted. However, the observed shift for both the O−H vibrations is marginally higher than the predicted for "B" and less than those predicted for "C". In the case of benzene−water π hydrogen-bonded complex, Zwier and co-workers have observed at least six transitions in the O−H stretching region which arise as a consequence of large-amplitude tumbling motion of water molecule.[1e] In the present case the FDIR spectrum in the O−H stretching region (Figure 3) shows two distinct transitions corresponding to the hydrogen-bonded and the free O−H vibrations, which implies that unlike the benzene−water case the water molecule is rigidly bound to phenylacetylene. The cyclic complex, structure C, has the water molecule rigidly bound to phenylacetylene with hydrogen-bonded and free O−H groups, and therefore is the probable structure. Further, the interaction of O−H group with the π electron density of acetylenic group perturbs the C≡C triple bond sufficiently to eliminate the Fermi mixing, resulting in single transition in the C−H stretching region (see Figure 2B). Additionally, as noted earlier, a relatively small blue shift of 14 cm^{-1} in the band origin transition of the phenylacetylene−water complex in comparison with the 50 cm^{-1} blue shift for the benzene−water complex suggests the water molecule may not be interacting with the benzene ring π electron density of phenylacetylene. On the other hand, interaction of the water O−H group with π electron density of acetylenic C≡C triple bond in the plane of the molecule would minimally perturb the electronic transition leading to a smaller shift. Shifts in both the electronic and the vibrational transitions thus provide overwhelming evidence for assigning the cyclic structure, C, to the observed phenylacetylene−water complex.

The observed structure of the phenylacetylene−water complex, C, is similar to the structure of the benzonitrile−water complex.[14] Ishikawa et al. have reported the FDIR spectrum of the benzonitrile−water complex, which shows two transitions in the O−H stretching region at 3614 and 3727 cm^{-1}, corresponding to the hydrogen-bonded and free O−H vibrations, respectively.[14a] Comparison of the shifts in the O−H stretching frequencies of the water complexes with phenylacetylene and benzonitrile suggests that the stability of the phenylacetylene−water complex is lower than the benzonitrile−water complex. This is can be rationalized on the basis of lower proton affinity of HC≡CH (641.4 kJ mol^{-1}) in comparison with HC≡N (772.3 kJ mol^{-1}).[15] It is interesting to note that the calculations predict the binding energies of complexes B and C to be almost equal; however, only the cyclic complex, C, was observed experimentally. This can be rationalized as follows: The ab initio calculations yield two minima for the benzene−water and acetylene−water complexes. The O−H···π hydrogen-bonded benzene−water and C−H···O hydrogen-bonded acetylene−water complex are the global minima and are observed experimentally.[1,2] Additionally, higher-energy local minima consisting of a C−H···O hydrogen-bonded benzene−water complex and a O−H···π hydrogen-bonded complex in the case of acetylene−water system are also predicted by ab initio calculations. The two higher-energy local minima of benzene−water and acetylene−water complexes cooperatively combine to stabilize the cyclic phenylacetylene−water complex.

Conclusions

In summary, a very small shift of +14 cm^{-1} in the electronic transition implies that the water does not perturb the benzene π system, significantly. The disappearance of the Fermi resonance transition in the acetylenic C−H stretching region with a very marginal shift of -3 cm^{-1}, implies that water interacts with the π electron density of the C≡C triple bond. The IR spectra in the O−H stretching region clearly indicate the presence of free and hydrogen-bonded O−H groups. These spectral features clearly establish the formation of cyclic complex between phenylacetylene and water. The structure of this complex neither resembles benzene-water nor acetylene-water complexes, even though phenylacetylene combines the features of benzene and acetylene. Formation of such a structure can be rationalized on the basis of cooperative interaction between C−H···O and O−H···π hydrogen bonds.

Note Added in Proof. Preliminary microwave results from Arunan and coworkers confirm the structure of the phenylacetylene-water complex derived in this work.

Acknowledgment. This material is based upon work supported by Department of Science and Technology (Grant No. SR/S1/PC-40/2003), Board of Research in Nuclear Sciences (Grant No. 2004/37/5/BRNS/398), and Council of Industrial and Scientific Research (Grant No. 01(1902)/03/EMR-II). The authors wish to thank Dr. D. K. Maity for his help with computations.

References and Notes

(1) (a) Engdahl, A.; Nelander, B. *J. Phys. Chem.* **1985**, *89*, 2860. (b) Wanna, J.; Menapace, J. A.; Bernstein, E. R. *J. Chem. Phys*. **1986**, *85*, 1795. (c) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, *257*, 945. (d) Gotch, A. J.; Zwier, T. S. *J. Chem. Phys*. **1992**, *96*, 3388. (e) Pribble, R. N.; Garrett, A. W.; Haber, K.; Zwier, T. S. *J. Chem. Phys.* **1995**, *103*, 531. (f) Gutowsky, H. S.; Emilsson, T.; Arunan, E. *J. Chem. Phys.* **1993**, *99*, 4883.

(2) (a) Engdahl, A.; Nelander, B. *Chem. Phys. Lett.* **1983**, *100*, 129. (b) Peterson, K. I.; Klemperer, W. *J. Chem. Phys.* **1984**, *81*, 3842.

(3) (a) Page, R. H.; Shen, Y. R.; Lee, Y. T. *J. Chem. Phys.* **1988**, *88*, 4621. (b) Pribble, R. N.; Zwier, T. S. *Science* **1994**, *265*, 75. (c) Riehn, C.; Lahmann, C.; Wassermann, B.; Brutschy, B. *Chem. Phys. Lett*. **1992**, *197*, 443. (d) Tanabe, S.; Ebata, T.; Fujii, M.; Mikami, N. *Chem. Phys. Lett*. **1993**, *215*, 347. (e) Fujii, A.; Patwari, G. N.; Ebata, T.; Mikami, N. *Int. J. Mass. Spectrom*. **2002**, *220*, 289.

(4) Singh, P. C.; Patwari, G. N. *Chem. Phys.* 2008.

(5) The IR OPO was calibrated by measuring the photo-acoustic spectrum of ambient water vapor. The absolute frequency calibration is within ±2 cm^{-1}.

(6) (a) King, G. W.; So, S. P. *J. Mol. Spectrosc*. **1971**, *37*, 543. (b) Dao, P-D.; Morgan, S.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1984**, *111*, 38.

(7) Stearns, J. A.; Zwier, T. S. *J. Phys. Chem. A* **2003**, *107*, 10717.

(8) (a) Matsuda, Y.; Ebata, T.; Mikami. N. *J. Chem. Phys.* **1999**, *110*, 8397. (b) Frost, R. K.; Hagemeister, F. C.; Arrington, C. A.; Schleppenbach, D.; Zwier, T. S.; Jordan, K. D. *J. Chem. Phys.* **1996**, *105*, 2605.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(10) Kim, S. K.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145.

(11) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, 1960.

(12) (a) Daunt, S. J.; Shurvell, H. F. *J. Mol. Spectrosc.* **1976**, *62*, 373. (b) Minejima, C.; Ebata, T.; Mikami, N. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1537.

(13) The deperturbation analysis was carried out for the 3324 and 3343 cm^{-1} peaks following the recipe given in ref 12. It predicts the energy difference between the zero-order vibrational states corresponding to the acetylenic C−H stretching vibration and the combination band of one quantum C≡C stretch and two quanta of C≡C−H out-of-plane bend to be 0.1 cm^{-1}. This implies that the stretching frequency of the unperturbed acetylenic C−H group is 3334 cm^{-1}.

(14) (a) Ishikawa, S.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **1999**, *110*, 9504. (b) Kryachko, E. S.; Nguyen, M. T. *J. Chem. Phys.* **2001**, *115*, 833. (c) Schafer, M.; Borst, D. R.; Pratt, D. W.; Brendel, K. *Mol. Phys.* **2002**, *100*, 3553.

(15) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data.* **1998**, *27*, 413.