Ab Initio Study of the Hydrogen Bonding between Pyrrole and Hydrogen Fluoride: A Comparison of NH⋯F and FH⋯π Interactions

1 AUTHOR:

Jyh-Chiang Jiang

National Taiwan University of Science and Te…

174 PUBLICATIONS   **2,606** CITATIONS

SEE PROFILE

π-hydrogen bonding between water and aromatic hydrocarbons at high temperatures and pressures

Seiya Furutaka and Shun-ichi Ikawa
Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Infrared OH stretching absorption of HDO isolated in aromatic hydrocarbons have been measured at temperatures of 473 and 523 K and at pressures in the 100–350 bar range. The peak frequencies are dependent on the solvents and their order, benzene>toluene>ethylbenzene>cumene >o-xylene~m-xylene>mesitylene, is exactly the same as the order for the ionization potentials of the hydrocarbons. Shifts of the frequencies from that of HDO in hexane, which was measured as a reference at the same temperature and pressure, were analyzed using a charge transfer theory for hydrogen bonding. Distances between the water molecule and a solvent phenyl ring were estimated to be 2.8±0.1 and 2.9±0.1 Å at 473 and 523 K, respectively. These values are consistent with a structure of a water–benzene complex determined by a jet-cooled microwave spectroscopy. These facts suggest that the π-hydrogen bond between water and aromatic hydrocarbons exists even at the high temperatures under pressure. © *2002 American Institute of Physics.*
[DOI: 10.1063/1.1484105]

I. INTRODUCTION

It has been known for a long time that aromatic hydrocarbons act as hydrogen bonding bases. This tendency was initially confirmed by infrared spectroscopy.[1] The spectrum of o-biphenylol (2-hydroxybiphenyl) in a dilute CCl_4 solution showed a doublet in the region of the first overtone of the OH stretching. The doublet was assigned to two different conformers in equilibrium produced by coupling of the hydroxyl group with the nearby phenyl ring. After that, many researchers have studied intra- or intermolecular interactions that aromatic hydrocarbons act as hydrogen bonding bases.[2,3] On the other hand, hydrogen bonding of water with benzene was indirectly confirmed by a ^{1}H–NMR method.[4–6] The hydrogen bond interaction usually shifts a proton resonance signal to lower fields, but the interaction with benzene shifts the proton signal of water to higher fields. This opposite shift has been interpreted in terms of the diamagnetic anisotropy of the aromatic π electrons. The hydrogen bonding interaction of water with aromatic hydrocarbons in the liquid state was also studied by infrared spectroscopy.[7–9] Furthermore, complexation of water with alkyl-substituted benzenes was studied in argon matrices by infrared spectroscopy.[10] Comparison of the peak wave numbers of water bands of the complexes and isolated water indicated π-hydrogen bond interactions between a water molecule and a phenyl ring. The ground-state microwave spectroscopy[11] and the resonant ion-dip infrared spectroscopy[12,13] of jet-cooled water–benzene mixture have revealed gas-phase structure of the water–benzene complex, in which the hydrogen atom of a water molecule points towards the benzene ring. *Ab initio* calculations have shown that the order of magnitude of the binding energy of the water–benzene complex is 7–12 kJ mol^{-1},[11,14–16] which is intermediate between the binding energy of van der Waals complexes and that of typical hydrogen-bonded complexes. Some authors claimed that the

rather large mutual solubility of water with aromatic hydrocarbons as compared with alkanes at ambient condition should be the result of a hydrogen-bondlike interaction between water and π electrons of an aromatic ring.[17,18]

This type of interaction involving π electrons has been considered to be important in biological systems.[19] The common constituents of globular proteins such as phenylalanine, tryptophan, and tyrosine possess an aromatic side-chain. When they encounter water molecules in internal hydrophobic cavities of the protein, π-hydrogen bonds may contribute to stabilize the local structure of the proteins.[20] On the other hand, if they lie on the surface of proteins, π-hydrogen bonds will contribute hydration energy.[21] Water at high temperatures and pressures, that is, the hydrothermal conditions, is prevalent in geochemistry and may have contributed to the origin of life.[22,23] To understand microscopic mechanism of the supercritical water oxidation of organic wastes, molecular dynamics simulations have been performed.[24–26] It has been pointed out that a benzene molecule can be preferably approached by the hydrogen atom of a water molecule under the supercritical condition.[26] The hydrogen bonds between water and aromatics at high temperatures and pressures, however, still remain largely unknown. In the previous papers,[27–31] we have reported the infrared spectra of HDO in some aromatic hydrocarbons at high temperatures and pressures, and found a certain correlation between the frequency shifts of HDO and the ionization potentials of the aromatic hydrocarbons at 373–473 K and 100 bar.[28] This fact suggests that the interaction of water and aromatic hydrocarbons in the high temperature–pressure mixtures can be described as π-hydrogen-bonding. In order to obtain further insight into the π-hydrogen-bonding, this paper deals with measurements of the infrared spectra of HDO in aromatic hydrocarbons at the extended range of temperature and pressure and reports
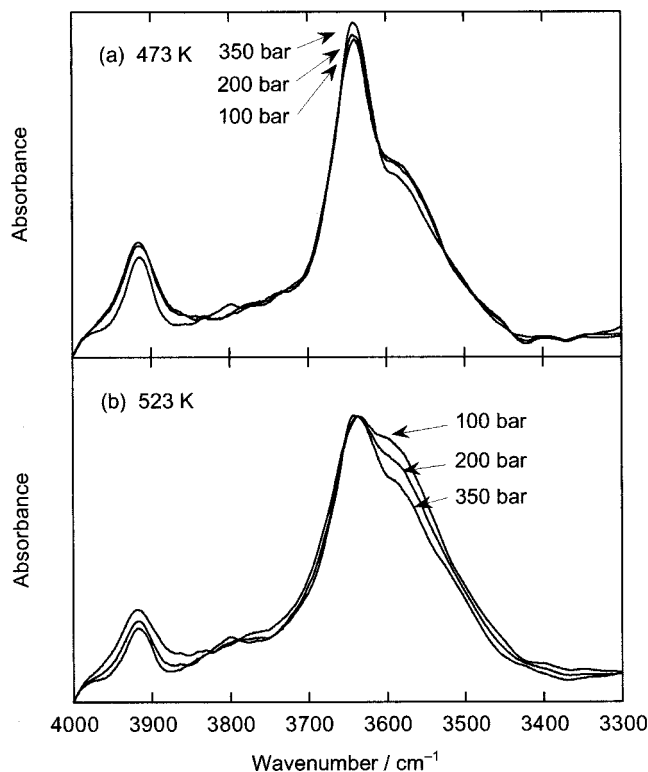
FIG. 1. Infrared absorption of HDO in cumene at 473 K (a) and 523 K (b) at a few pressures.

FIG. 2. Infrared absorption of HDO in various alkyl-substituted benzenes at 473 K and 100 bar.

an analysis of the frequency shifts on the bases of a charge-transfer model.

II. EXPERIMENT

A high-pressure cell used has been described in detail elsewhere.[30,31] The optical path length of a sample was 1 mm. Spectroscopic grade benzene, toluene, ethylbenzene, cumene, o-xylene, m-xylene, mesitylene, and hexane from Nakarai Tesque (Japan) and deuterium oxide (99.9% D) from CEA (France) were used as received. The water specimens were mixtures of H_2O and D_2O with a ratio of 1:10 and 1:20. Then the ratios of the isotopic species H_2O, HDO, and D_2O in these specimens were estimated to be 1:20:100 or 1:40:400. Therefore, contribution of H_2O to the infrared OH stretching absorption can be approximately neglected as compared with that of HDO, and the observed OH band is assigned only to HDO. A syringe pump of liquid chromatography was used for transmitting compressed liquids of hydrocarbons into the cell in which a certain amount of the water specimens had been put in advance and its level adjusted so as to be slightly below the optical path. Infrared absorption of the hydrocarbon-rich phase was observed with a BOMEM DA3 Fourier-transform spectrometer equipped with a CaF_2 beamsplitter and a mercury–cadmium–telluride detector. The spectral measurements were performed with 2 cm^{-1} resolution at sample temperatures 473 and 523 K and pressures in the 100–350 bar range. The phase equilibrium of the mixture was confirmed by the spectrum that was unchanged for at least 1 h. Absorbance of HDO in the OH
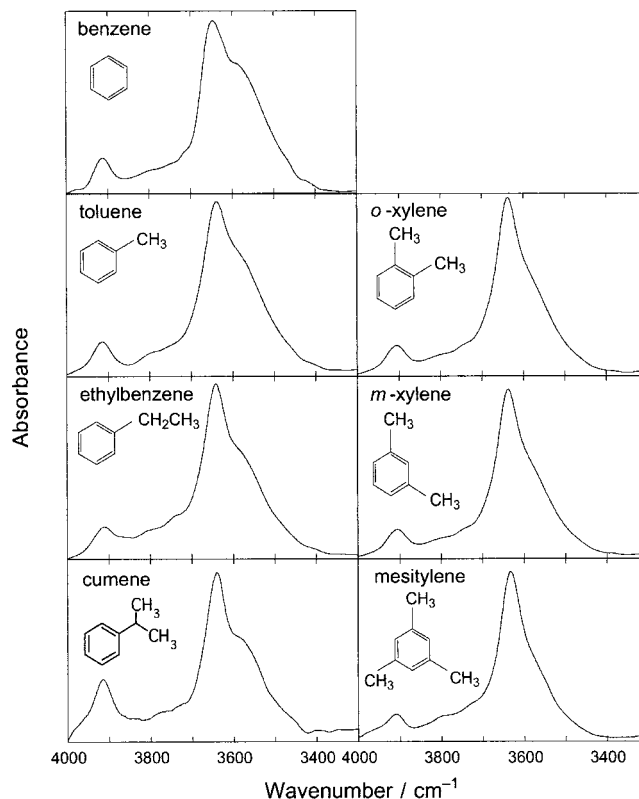
stretching region was obtained by subtracting the spectrum of neat hydrocarbon measured at the same condition.

III. RESULTS AND DISCUSSION

Figure 1 shows the OH stretching absorption of HDO dissolved in cumene at 473 and 523 K at a few pressures. Bands at about 3640 cm^{-1} and 3580 cm^{-1} are assigned to hydrogen-bond-free OH groups and hydrogen-bonded OH groups, respectively.[27,28] It should be mentioned here that the term "hydrogen-bonded" means "hydrogen-bonded to water" and the hydrogen-bond-free groups are the ones believed to be bonded to the aromatic hydrocarbons probably through a π-hydrogen bonding. A band at about 3910 cm^{-1} is assigned to a combination band of D_2O.[29] Infrared absorption of HDO observed in all the solvents used are very similar in profile as seen in Fig. 2. Positions of the hydrogen-bond-free bands, however, vary with different solvents. The peak frequencies are in the following order, benzene>toluene>ethylbenzene>cumene>o-xylene $\sim m$-xylene>mesitylene. This is exactly the same order as that of the vertical ionization potentials[32] of the hydrocarbons as shown in Fig. 3. The ability of the hydrocarbons as the hydrogen-bond acceptor will be related to their electron-release tendency which is represented by the ionization potential. Another intriguing point is that the peak frequencies of the monomeric HDO in benzene, 3649–3651 cm^{-1} in the 473–523 K range, are near to that of a water–benzene complex, 3650 cm^{-1},[12] which was observed for a jet-cooled cluster with resonant ion-dip infrared spectroscopy. This agreement suggests that the monomeric water in benzene at high temperature and pressure undergoes a similar interaction to
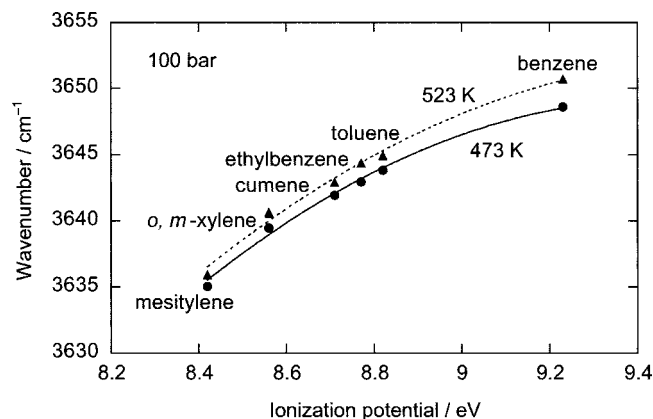
FIG. 3. The correlation between OH stretching frequencies of HDO and the vertical ionization potential of solvent aromatic hydrocarbons.
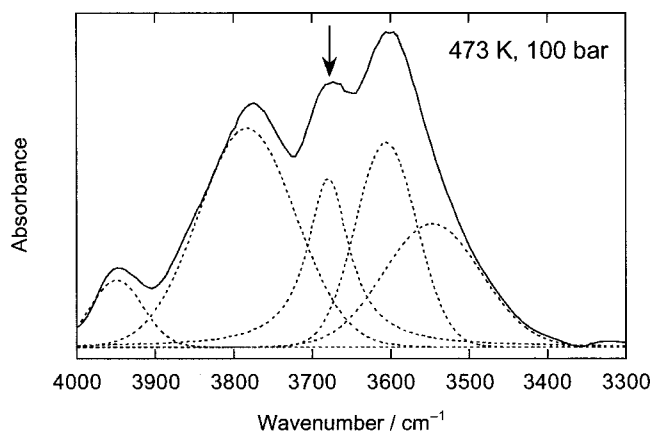

FIG. 4. Infrared absorption of HDO in hexane at 473 K and 100 bar. The arrow indicates the ν_F band, the Q branch of HDO molecules free from water–water association.

that in the low-temperature complex, in which water forms a hydrogen bond with benzene, with one of its hydrogen atoms pointing toward the center of the aromatic ring.[11] In this configuration, the π-electron of the benzene ring is thought to act as a hydrogen-bond acceptor.

To characterize further the water–hydrocarbon interaction in the high-temperature–pressure mixtures, we analyzed correlation between the OH stretching frequencies and the ionization potentials of aromatic hydrocarbons using a charge-transfer model for hydrogen bonding by Ratajczak and Orville-Thomas.[33] On the basis of Mulliken's second-order perturbation calculation for loose 1:1 charge-transfer complexes,[34] they derived the following relationship between the frequency shift of an X–H stretching band, $\Delta\nu(\text{X–H})$, and the vertical ionization potential, I_D, of an electron donor molecule (aromatic hydrocarbon in the present study)

$$[\Delta\nu(\text{X–H})]^{-1} = \frac{a}{\beta_0^2}(I_D - E_A - C), \tag{1}$$

where, E_A is the electron affinity of the electron acceptor molecule (water in the present study), C is the difference in stabilization energies between the excited and ground states, a is a constant for structurally similar hydrogen-bonded complexes, and β_0 is related to the overlap integral between the donor and acceptor orbitals. For convenience, Eq. (1) is rewritten as

$$[\Delta\nu(\text{X–H})]^{-1} = m \cdot I_D + n, \tag{2}$$

where

$$m = a \cdot \beta_0^{-2}, \tag{3}$$

$$n = -a \cdot \beta_0^{-2} \cdot (E_A + C) = -m \cdot (E_A + C). \tag{4}$$

Thus, a linear relationship is expected between $(\Delta\nu)^{-1}$ and I_D.

The frequency shift $\Delta\nu$ is given by $\Delta\nu = \nu_F - \nu_B$, where ν_F and ν_B, respectively, are OH stretching frequencies free from and influenced by the charge transfer effect. As a value of ν_F, the OH stretching frequency of HDO in hexane at the same temperature and pressure as for ν_B is used. It is assumed that ν_F involves a similar interaction to that in aro-

matic hydrocarbons except the charge transfer effect. Figure 4 shows infrared absorption of HDO in hexane at 473 K and 100 bar. The profile of the OH absorption is remarkably different from those in aromatic hydrocarbons. The bands at around 3680 and 3600 cm^{-1} are assigned to the hydrogen-bond-free and hydrogen-bonded species by the analogy with the OH bands in aromatic hydrocarbons. The band at about 3780 cm^{-1} is assigned to a vibration-rotation transition of hydrogen-bond-free HDO, by analogy with the peak of frequency measured in an argon matrix.[35] The corresponding bands can be seen in the spectra in Fig. 2, but their relative intensities are significantly smaller than that of 3780 cm^{-1} band in hexane. This fact indicates that the rotational motion of the water molecule in hexane is significantly free as compared with that in aromatic hydrocarbons, and may be quasi-free as in decane and octane at ambient condition.[36,37] This is probably due to absence of a hydrogen-bondlike interaction between water and hexane, being different from the interaction between water and aromatic hydrocarbons. It should be noted here that the 3780 cm^{-1} band assigned to the vibration-rotation transition should have a lower frequency counterpart with roughly the same broadening but less intensity. This component can be seen by a band decomposition shown by dotted lines in Fig. 4. Details of the band shape analysis will be reported elsewhere.

The resulting values of $(\Delta\nu)^{-1}$ are plotted against I_D in Fig. 5. As expected above, the plots are approximately linear for every experimental condition. This fact indicates that the interaction between water and aromatic hydrocarbons in the mixtures at high temperatures and pressures can be described as the charge-transfer interaction or the π-hydrogen bonding.

Using the E_A value of water, 1.2 eV,[38] the distance r between water and the phenyl ring can be estimated from the experimentally determined m and n values on the assumption that r is independent of the aromatic hydrocarbons used in the present study. From Eqs. (3) and (4), we obtain

$$\frac{n}{m} + E_A = -C. \tag{5}$$

The stabilization energy of the excited state, or the charge transfer state, is approximately given by the Coulomb energy
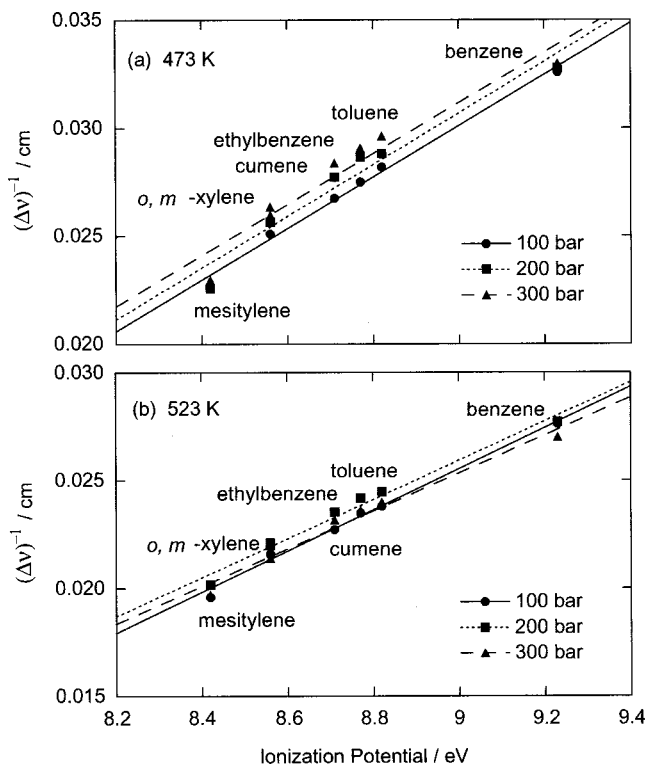
FIG. 5. Plots of the frequency shifts of the OH stretching of HDO against the ionization potentials of the solvent aromatic hydrocarbons at 473 K (a) and 523 K (b) at 100–300 bar.

of the ion pair and much larger than that of the ground state.[39] Therefore, C is approximately given by $-q^2/(4\pi\epsilon_0 r)$, where q is the elementary electric charge ($q = 1.602 \times 10^{-19}$ C) and ϵ_0 is the electric permittivity of vacuum ($\epsilon_0 = 8.854 \times 10^{-12}$ F m^{-1}). Consequently, the distance or, strictly speaking, the charge transfer distance r between water and the aromatic hydrocarbon is given by the following relationship:

$$r = \frac{q^2}{4\pi\epsilon_0[-(n/m)-E_A]}.$$ (6)

Using the values of n/m estimated from the slope and the intercept of the plots in Fig. 5, r is estimated to be 2.8 ± 0.1 and 2.9 ± 0.1 Å at 473 and 523 K, respectively. The r values are almost independent of pressure in the 100–350 bar range. Figure 6 shows a schematic of a water–benzene complex, where a cross ($\times$) represents the center of the benzene ring. In the MP-2 optimized structure,[15] the distance from $\times$ to the hydrogen (H) involved in the π-hydrogen bond is 2.302 Å, and the distance to the oxygen (O) of a water molecule is 3.210 Å, which is in fair agreement with the experimental value of 3.347 Å determined from jet-cooled microwave spectra.[11] Considering the charge-transfer from the π-orbital of the aromatic ring to the antibonding orbital of the OH bond, it seems reasonable that the r values are in the middle of the two explicitly defined distances mentioned above. Therefore, the present experimental result indicates that the concept of π-hydrogen bonding is effective for describing the water–aromatic hydrocarbon interaction in the high-temperature–pressure mixtures.
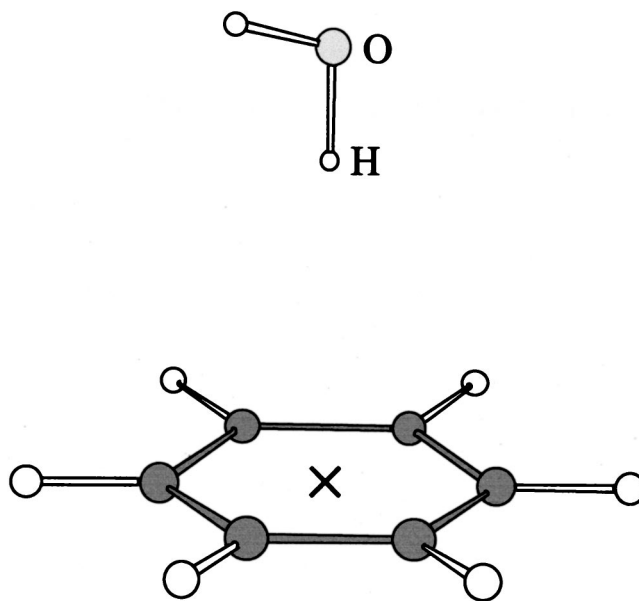

FIG. 6. Schematic of a water–benzene complex.

IV. CONCLUSION

Infrared spectra of HDO dissolved in various aromatic hydrocarbons have been measured at 473 and 523 K and pressures in the 100–350 bar range. The OH stretching frequencies assigned to HDO monomers, which are free from water–water association, are in the following order: benzene>toluene>ethylbenzene>cumene>o-xylene $\sim m$-xylene>mesitylene. We have analyzed a correlation of the OH stretching frequencies with the ionization potentials of the solvent hydrocarbons using a charge transfer theory for hydrogen bonding. The charge transfer distance between the water molecule and the solvent aromatic ring estimated by that model is consistent with the structure of a water–benzene complex obtained by a jet-cooled microwave spectroscopy[13] and theoretical calculations.[15] This fact suggests that the π-hydrogen bond between water and aromatic hydrocarbons exists even at high temperatures under pressure.

[1] O. R. Wulf, U. Liddel, and S. B. Hendricks, J. Am. Chem. Soc. **58**, 2287 (1936).
[2] G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (Freeman, San Francisco, 1960).
[3] Z. Yoshida and E. Osawa, J. Am. Chem. Soc. **87**, 1467 (1965).
[4] A. D. Cohen and C. Reid, J. Chem. Phys. **25**, 790 (1956).
[5] M. Baron, Anales. Asoc. Quim. Argentina **67**, 203 (1979).
[6] M. Nakahara and C. Wakai, Chem. Lett. **1992**, 809.
[7] E. Gentric, A. La Narvor, and P. Saumagne, C. R. Acad. Sci. Paris, Ser. C **270**, 1053 (1970).
[8] O. D. Bonner and Y. S. Choi, J. Phys. Chem. **78**, 1723 (1974).
[9] J. Cz. Dobrowolski and M. H. Jamróz, J. Mol. Struct. **293**, 147 (1993).
[10] A. Engdahl and B. Nelander, J. Phys. Chem. **91**, 2253 (1987).

[11] S. Suzuki, P. G. Green, R. E. Bumgarner, S. Dasgupta, W. A. Goddard III, and G. A. Blake, Science **257**, 942 (1992).

[12] R. N. Pribble and T. S. Zwier, Faraday Discuss. **97**, 229 (1994).

[13] H.-D. Barth, K. Buchhold, S. Djafari, B. Reimann, U. Lommatzsch, and B. Brutschy, Chem. Phys. **239**, 49 (1998).

[14] S. Y. Fredericks, K. D. Jordan, and T. S. Zwier, J. Phys. Chem. **100**, 7810 (1996).

[15] D. Feller, J. Phys. Chem. **103**, 7558 (1999).

[16] P. Tarakeshwar, H. S. Choi, S. J. Lee, J. Y. Lee, K. S. Kim, T.-K. Ha, J. H. Jang, J. G. Lee, and H. Lee, J. Chem. Phys. **111**, 5838 (1999).

[17] S. Goldman, Can. J. Chem. **52**, 1668 (1974).

[18] P. Ruelle, M. Buchmann, H. Nam-Tran, and U. W. Kesselring, J. Comput.-Aided Mol. Des. **6**, 431 (1992).

[19] T. Steiner and G. Koellner, J. Mol. Biol. **305**, 535 (2001).

[20] J. L. Atwood, F. Hamada, K. D. Robinson, G. W. Orr, and R. L. Vincent, Nature (London) **349**, 683 (1991).

[21] T. Steiner, A. M. M. Schreurs, J. A. Kanters, and J. Kroon, Acta Crystallogr., Sect. D: Biol. Crystallogr. **54**, 25 (1998).

[22] B. R. T. Simoneit, Geochim. Cosmochim. Acta **57**, 3241 (1993).

[23] T. B. Brill, J. Phys. Chem. A **104**, 4343 (2000).

[24] J. Gao, J. Am. Chem. Soc. **115**, 6893 (1993).

[25] P. T. Cummings, A. A. Chialvo, and H. D. Cochran, Chem. Eng. Sci. **49**, 2735 (1994).

[26] J. Zhou, W. Wang, and C. Zhong, Chinese J. Chem. Eng. **9**, 196 (2001).

[27] S. Furutaka and S. Ikawa, J. Chem. Phys. **108**, 1347 (1998).

[28] S. Furutaka and S. Ikawa, J. Chem. Phys. **108**, 5159 (1998).

[29] S. Furutaka and S. Ikawa, J. Chem. Phys. **113**, 1942 (2000); **113** 8390(E) (2000).

[30] S. Furutaka and S. Ikawa, Fluid Phase Equilib. **185**, 379 (2001).

[31] S. Furutaka, H. Kondo, and S. Ikawa, Bull. Chem. Soc. Jpn. **74**, 1775 (2001).

[32] J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasinc, R. M. Wightman, and J. K. Kochi, J. Am. Chem. Soc. **106**, 3968 (1984).

[33] H. Ratajczak and W. J. Orville-Thomas, J. Mol. Struct. **19**, 237 (1973).

[34] R. S. Mulliken, J. Am. Chem. Soc. **74**, 811 (1952).

[35] R. M. Bentwood, A. J. Barnes, and W. J. Orville-Thomas, J. Mol. Spectrosc. **84**, 391 (1980).

[36] M. P. Conrad and H. L. Strauss, Biophys. J. **48**, 117 (1985).

[37] M. P. Conrad and H. L. Strauss, J. Phys. Chem. **91**, 1668 (1987).

[38] W. J. Griffiths and F. M. Harris, Org. Mass Spectrom. **22**, 559 (1987).

[39] R. S. Mulliken and W. B. Person, *Molecular Complexes* (Wiley–Interscience, New York, 1969).