Chem. Rev. **2000,** *100,* 4145–4185

Molecular Clusters of π-Systems: Theoretical Studies of Structures, Spectra, and Origin of Interaction Energies

Kwang S. Kim,* P. Tarakeshwar, and Jin Yong Lee

National Creative Research Initiative Center for Superfunctional Materials, Department of Chemistry, Division of Molecular and Life Sciences, Pohang University of Science and Technology, San 31, Hyojadong, Pohang 790-784, Korea

Received December 22, 1999

Contents

1. Introduction

Much interest has been evinced on the properties of weakly bound van der Waals complexes of π-systems because of their utility in diverse fields (Figure 1).[1−14] Theoretical calculations of these properties have generally been marred by an inherent floppiness of these weakly bound complexes.[7−15] Hence, characterization of the global minimum structure of these weakly bound complexes has been a challenging problem, as one is confronted with a potential-energy surface which in most cases is shallow and anharmonic.[16] The problem becomes more acute for large clusters, wherein several isoenergetic and stable configurations exist. When the anisotropy of the intermolecular potential in the ground vibrational state is fairly large, the complex can be localized to a valley corresponding to the global minimum. In any case, one of the major bottlenecks in the theoretical characterization of these systems has been the available computational resources.

The spectacular progress in the development of highly efficient computational algorithms and computer hardware has dramatically altered the scenario on the theoretical front in the last couple of years. Thus, complexes which were once considered intractable can be theoretically characterized to a high degree of accuracy. These characterizations include the elucidation of the geometrical features of complexes which cannot be obtained experimentally, the determination of the interaction energies of these complexes which are important in understanding their formation and stability, and the interpretation of the experimental vibrational and rotational spectra.

Experimentally and theoretically, one of the vexing issues of intermolecular interactions is on how an interplay of attractive and repulsive forces govern the interaction of two or more isolated molecules. When one of the molecules involved has π-bonds, this interplay attains a lot of significance not only on the interaction energies but also on the geometries exhibited by these complexes. Apart from the diffuse nature of the electron density in the π-system, a number of other factors also gain importance. These factors include the nature of substituents (electron-withdrawing or electron-donating), the presence of heteroatoms (oxygen or nitrogen) either as substituents or as constituents of the aromatic rings, and the presence of additional rings (polycyclic π-systems).

Some of the earliest theoretical successes in the study of van der Waals complexes have been achieved on systems containing π-systems, both aromatic and olefinic. It should be noted that molecules such as HCN and H_2CO also contain π-bonds, but the π-complexes formed by these molecules are not equilibrium structures. What makes the complexes of these π-systems interesting are that most of the π-systems are excellent chromophores and hence spectroscopically accessible. As a result, one can readily characterize the changes resulting from an interaction of

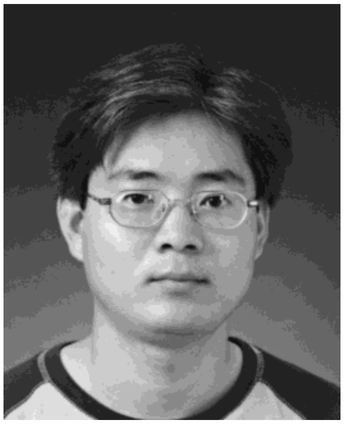
---

* To whom correspondence should be addressed. Telephone: +82 54 279 2110. Fax: +82 54 279 8137. E-mail: kim@postech.ac.kr. Web page: http://csm.postech.ac.kr.

10.1021/cr990051i CCC: \$35.00

Kwang S. Kim was born in 1950 in Seoul, Korea. He received his undergraduate degree in applied chemistry and his master's degree in chemical engineering from Seoul National University. He also received his master's degreee in physics from Korea Advanced Institute of Science and Technology. He obtained his Ph.D. degree in 1982 under Professor Henry F. Schaefer III at the University of California in Berkeley. He then spent some time as an IBM postdoctoral fellow with Professor Enrico Clementi and as a Research Assistant Professor at Rutgers University. In 1988, he joined Pohang University of Science and Technology (POSTECH) in Korea as an Assistant Professor and subsequently became a Professor in 1994. He is currently also the Director of the National Creative Research Initiative Center for Superfunctional Materials. Apart from being a member of the ACS, APS, and AAAS, he is a member of the Korea Academy of Science and Technology. He is currently an Associate Editor of the *Bulletin of the Korean Chemical Society*. His fields of research include theoretical investigations of intermolecular interactions, clusters, molecular recognition, and molecular devices. Professor Kim has authored or co-authored more than 100 papers in various fields of chemistry.

P. Tarakeshwar was born in 1967 in Kharagpur, India. He received his undergraduate and master's degrees in chemistry from the Orissa University of Agriculture and Technology (Bhubaneswar, India) and the University of Roorkee (Roorkee, India), respectively. He obtained his Ph.D. degree in 1994 under Professor S. Manogaran from the Indian Institute of Technology, Kanpur. He then worked as a scientist in drug design in Torrent Pharmaceuticals (Admedabad, India). In 1997, he joined Professor Kim's group in Pohang as a postdoctoral fellow and is currently a Research Assistant Professor in the center for superfunctional materials. His research interests include the development of ab initio force fields and detailed theoretical investigations of intermolecular interactions and molecular clusters containing π systems. He is also interested in understanding the role of catalysts in organic chemistry and molecular mechanisms of diseases.



Jin Yong Lee was born in 1969 in Koryong, Korea, and received both his undergraduate and master's degrees in chemistry from Pohang University of Science and Technology. He obtained his Ph.D. degree in 1997 under Professor Kwang S. Kim. After spending a year with Professor David Chandler at the Unversity of California, Berkeley, as a Korean Research Foundation (KRF) postdoctoral fellow, he returned to Pohang in 1998, where he is currently working as Senior Research Scientist in the Center for Superfunctional Materials. He received a Young Scientist Award from the KRF in 1994. He has varied research interests ranging from theoretical investigations of van der Waals clusters, nonlinear optical properties, and reaction dynamics to organic and biochemical reaction mechanisms.

the π-system with another system. Indeed, this is one of major reasons for the availability of a large amount of experimental data on these complexes. Since subtle variations of the ring substituents lead to significant changes in the reactivity, they are excellent model systems to study the reactivity of molecules in the gas phase. Before we go into the details of the nature of the intermolecular interactions and their influence on the geometries, energetics, vibrational frequencies, and charges of these complexes, it is useful to recall that attractive forces are mainly comprised of electrostatic, dispersive, and inductive interactions while the repulsive forces are mostly due to exchange repulsions. Each of these components has a different physical origin, magnitude, and directionality. Thus, electrostatic forces result from interactions between the permanent electric multipole moments of the complex partners; induction forces result from interactions of the permanent electric multipole moment of one monomer with the electric multipole moment induced in the other monomer; dispersion forces result from the mutual polarization of the electron densities of the two interacting monomers; repulsive forces result from the Pauli exclusion principle, which prevents the electrons of one monomer from penetrating into the occupied space of the other monomer. This exchange repulsion increases with increasing overlap and is always destabilizing. In the course of the review, we illustrate the importance of the effects of these repulsive interactions on the properties exhibited by complexes containing π-systems. In particular, we emphasize that the geometries and energies of these complexes are more a result of the system trying to minimize the destabilizing repulsive interaction than an increase in the stabilizing attractive interactions. Additionally, we show how theoretical calculations, in contrast to tedious experimental observations, help examine the changes in the nature of the interaction as the level of complexity and the number of intermolecular interactions are increased in a systematic way.

Some of the pertinent issues which will be addressed in the course of this review are the following: (i) What are the similarities/differences between complexes formed from olefinic and aromatic π-sys-

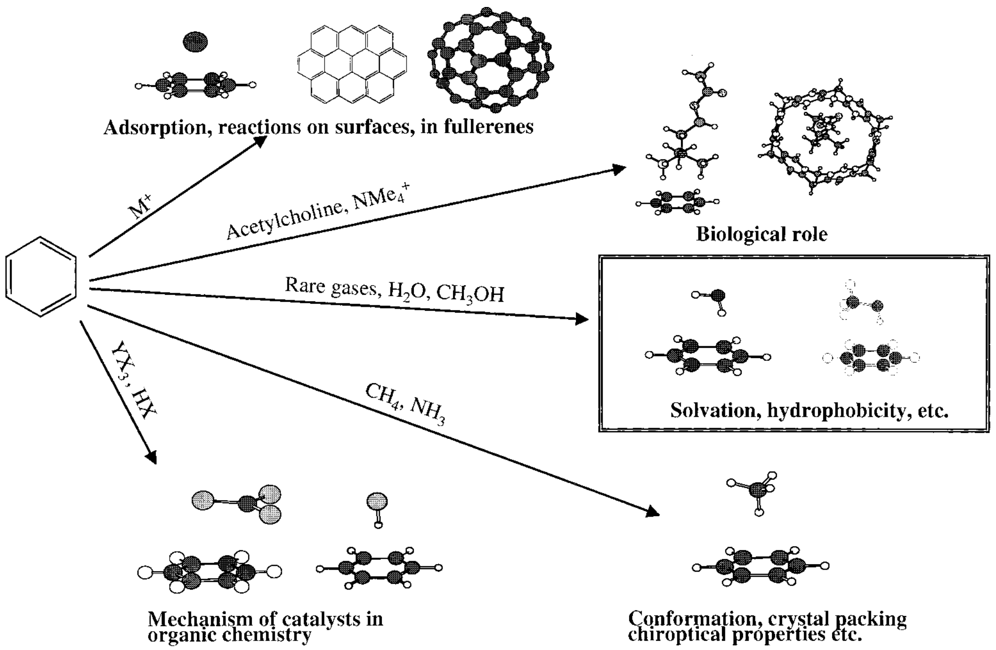


Figure 1. Examples of situations where theoretical calculations of complexes containing π-systems might prove to be useful.

tems? (ii) How does the substituent, which modulates the charge distributions of the aromatic or olefinic molecule, influence the geometries, interaction energies, and vibrational frequencies of these π-complexes? (iii) How does the interplay of the repulsive and attractive forces govern the binding of different molecules to these π-complexes? (iv) What are the major differences between conventional H-bonds and the weak bonds formed with these π-systems? (v) The extent of charge reorganization in the formation of these weakly bound π-complexes. (vi) The relative contribution of intra- and intermolecular effects on the reactivity observed in these complexes. (vii) A related but vital issue is the aspect of these π-complexes behaving as precursors of chemical reactions. This issue is particularly highlighted with regard to electrophilic aromatic substitution reactions. In contrast to the interaction of π-systems with isolated molecules (M), their interaction with larger clusters of molecules (M_n) brings to fore a number of significant issues. Thus, in addition to the interaction of the π-system with each of the individual molecules in the cluster, the interaction between the molecules in the clusters also become significant. Thus, it would be interesting to examine how the presence of both π−M and M−M interactions influence the resulting properties of the complex.

In the following sections, after a brief overview of the theoretical methods, the salient results obtained from high-level ab initio calculations for a wide variety of π-complexes will be discussed. In the case of the larger π-systems, the discussion also includes results obtained from empirical and semiempirical calculations. The emphasis of the review to a large extent is on the origin of some of the experimental features (geometries, energies, frequencies) of these π-complexes. However, in the course of the review, we also focus on the state-of-the-art in the theoretical characterization of these π-complexes.

2. Theoretical Methods

A wide variety of theoretical methods have been employed to investigate the complexes reported in this review. These methods include Monte Carlo and molecular dynamic simulations using a wide variety of potentials.[17−22] For more details on potentials, see the review of Engkvist, Astrand, and Karlström in this volume. The semiempirical method developed by Claverie et al. also merits mention because of its widespread usage by a number of groups carrying out calculations on clusters.[23−26] This method is based on the "exchange perturbation theory". Thus, at the second order of this treatment, the interaction energy is obtained as a sum of four terms: electrostatic, polarization, dispersion, and short-range repulsion. The representation of each of these contributions by simple analytical formulas helps this method give a reliable description of the interactions for all intermolecular distances. Since the repulsive term includes the influence of electron population variation on the van der Waals radius of each atom, there are some problems in the description of the hydrogen atom. These problems have been mitigated to some extent by taking into account the polarization terms of order n ($n > 3$) and the term of polarization exchange. Though these empirical and semiempirical methods have been quite useful in the description of these complexes, detailed ab initio calculations have been instrumental in obtaining a clear overview of the structure, interaction energies, and vibrational frequencies of these complexes.

Two different approaches have generally been employed to carry out ab initio calculations of these complexes. These include the supermolecular (SM) variational method (wherein the interaction energy is the difference between the energy of the cluster and the energies of the isolated systems) and the perturbational method[27] (wherein the interaction energy is computed directly as a sum of physically distinct contributions: *electrostatics, exchange, dispersion, and induction*). While the accuracy of both the supermolecular and perturbational approaches depends on the size of the basis set used and the level of the correlation employed, the perturbational approach suffers from more practical problems. For large systems, most of the available programs can evaluate only the simpler of the various possible energy contributions consituting the total interaction energy.

Given the several practical advantages of the supermolecular approach over the perturbational approach, which include the wide availability of a large number of programs,[28−33] it has been extensively employed in the evaluation of the intermolecular energies, geometries, and harmonic vibrational frequencies. Since dispersive interactions have a vital contribution to the total interaction energy exhibited by these π-complexes, it becomes important to explicitly include electron correlation in the calculations. In the past, the widely used methods which took into account the effect of electron correlation were the Møller−Plesset (MP),[34] configuration interaction (CI),[35] and the coupled-cluster (CC) methods.[36,37] However, the recent advent of density functional theory (DFT) based methods,[38−40] which allow one to include electron correlation at lower computational costs and also obtain reasonable results, has led to its widespread usage in a number of calculations. The results obtained from DFT methods are in most cases satisfactory, but their accuracy to a large extent is dependent on how good the functionals are suitable for the particular system under consideration.

Even though there are some practical problems with the perturbational approach, it is the only available recourse toward understanding the nature and origin of intermolecular interactions involving π-systems.[41,42] In this context, the symmetry adapted perturbation theory (SAPT) program[43] has been extensively employed in the recent past in the investigation of the interaction energies and its components for a number of systems.[43−58] An efficient use of SAPT involves the evaluation of the interaction energy on the geometry of the energy minimum of the complex.

At the suggestion of one of the referees, we briefly recapitulate the salient features of SAPT.[42,43] In SAPT, the dimer is described in zeroth order by the product of wave functions of unperturbed monomers. The penetration effects are included in SAPT by keeping the interaction potential in the nonexpanded form. The exchange effects are included by acting on the wave function with operators interchanging electrons between the interacting systems. Since the monomers' wave functions (i.e., ψ_0 is unavailable) are not known for many-electron systems, the most practical approximations are the Hartree−Fock determinants Φ_x. The intramonomer correlation contribution is then obtained in a perturbative way, i.e., double-perturbation approach. Møller−Plesset partitioning is used to decompose the monomer Hamiltonians H_A and H_B into the Fock operator F_X, X = A or X = B, and the intramonomer correlation operator $W_X = H_X - F_X$. The total Hamiltonian decomposes then as $H = F + V + W$, where $F = F_A + F_B$ is the new unperturbed operator, $W = W_A + W_B$ is the operator accounting for intramonomer correlation effects, and V is the (nonexpanded) intermolecular interaction operator. The zeroth-order function is given by the product of the Hartree−Fock determinants:

$$\Phi_0 = \Phi_A \Phi_B \tag{1}$$

The double-polarization expansion for the wave function and interaction energy is obtained by the Taylor expansion around $\lambda = 0$ and $\mu = 0$ of the functions $E(\lambda,\mu)$ and $\Phi(\lambda,\mu)$ defined for each λ and μ by the equation

$$(F + \lambda V + \mu W)\Phi(\lambda,\mu) = E(\lambda,\mu)\Phi(\lambda,\mu) \tag{2}$$

The corrections of the double-symmetrized Rayleigh−Schrödinger theory are defined by an analogous Taylor expansion of the function

$$\mathrm{E}(\lambda,\mu) = \frac{\langle \Phi(0,\mu) \lambda V A\, \Phi(\lambda,\mu)\rangle}{\langle \Phi(0,\mu) A\, \Phi(\lambda,\mu)\rangle} \tag{3}$$

The resulting double SAPT series for the interaction energy can be written as

$$E_{\mathrm{int}}^{\mathrm{SAPT}} = \sum_{n=1}^{\infty}\sum_{i=1}^{\infty}(E_{\mathrm{pol}}^{(ni)} + E_{\mathrm{exch}}^{(ni)}) \tag{4}$$

where n and i denote the order with respect to V and W, respectively. In each order the electrostatic part, given by the standard Rayleigh−Schrödinger expansion, and the exchange part which results from tunneling of electrons between interacting systems are separated. Thus, the intramonomer correlation contribution through the kth order can be represented as

$$\epsilon_{\mathrm{pol}}^{(n)}(k) = \sum_{l=1}^{k} E_{\mathrm{pol}}^{(nl)} \tag{5}$$

and similarly for the exchange components.

The SAPT components can be classified either as describing the interactions at the Hartree−Fock level or as the corrections for the effects of electron correlation. The former components can be related to the supermolecular Hartree−Fock energy $E_{\mathrm{int}}^{\mathrm{HF}}$

$$E_{\mathrm{int}}^{\mathrm{HF}} = E_{\mathrm{pol}}^{(10)} + E_{\mathrm{exch}}^{(10)} + E_{\mathrm{ind,resp}}^{(20)} + E_{\mathrm{exch-ind,resp}}^{(20)} + \delta_{\mathrm{int,resp}}^{\mathrm{HF}} \tag{6}$$

where “ind” denotes the induction component and “resp” indicates that a given component has been computed including the coupled Hartree−Fock response for the perturbed system. The $\delta_{\mathrm{int,resp}}^{\mathrm{HF}}$ collects all induction and exchange−induction terms of order higher than the second. The total interaction energy is then computed in a hybrid approach as

$$E_{\mathrm{int}}^{\mathrm{SAPT}} = E_{\mathrm{int}}^{\mathrm{HF}} + E_{\mathrm{SAPT}}^{\mathrm{corr}} \tag{7}$$

where $E_{\rm SAPT}^{\rm corr}$ is the sum of the correlation components of SAPT. Though this ansatz is not rigorous, the incorporation of the higher order induction and exchange−induction contributions leads to a significant improvement in the calculated energies. The correlation contribution to the interaction energy is obtained as

$$E_{\rm SAPT}^{\rm corr} = \epsilon_{\rm pol,resp}^{(1)}(3) + \epsilon_{\rm exch}^{(1)}(CCSD) + E_{\rm disp}^{(20)} + \epsilon_{\rm disp}^{(2)}(2) + E_{\rm exch-disp}^{(20)} + {}^{t}E_{\rm ind}^{(22)} + {}^{t}E_{\rm exch-disp}^{(22)} \quad (8)$$

where $\epsilon_{\rm exch}^{(1)}$(CCSD) incorporates intramonomer correlation at the level of the coupled-cluster single and double excitations and ${}^{t}E_{\rm ind}^{(22)}$ is the "true" correlation part of $E_{\rm ind}^{(22)}$. The exchange part of this component is estimated from

$$ {}^{t}E_{\rm exch-ind}^{(22)} \approx E_{\rm exch-ind,resp}^{(20)} \frac{{}^{t}E_{\rm ind}^{(22)}}{E_{\rm ind,resp}^{(20)}} \quad (9)$$

The evaluation of some of these components was computationally not feasible for the larger benzene complexes. In those complexes, the correlation contribution to the interaction energy is obtained as

$$E_{\rm SAPT}^{\rm corr} = \epsilon_{\rm pol,resp}^{(1)}(2) + \epsilon_{\rm exch}^{(1)}(2) + E_{\rm disp}^{(20)} + E_{\rm exch-disp}^{(20)} \quad (10)$$

We have observed that the total SAPT interaction energy obtained in such a fashion is equivalent to the basis set superposition error (BSSE)-corrected supermolecular second-order Møller−Plesset perturbation (MP2) interaction energy.

To facilitate the discussion of these interaction energy components, we have found it useful to collate both the Hartree−Fock and correlation components of each energy term and represent the total SAPT interaction energy $E_{\rm int}^{\rm SAPT}$ as

$$E_{\rm int}^{\rm SAPT} = E_{\rm pol}^{(1)} + E_{\rm exch}^{(1)} + E_{\rm ind}^{(2)} + E_{\rm exch-ind}^{(2)} + E_{\rm disp}^{(2)} + E_{\rm exch-disp}^{(2)} + \delta_{\rm int,resp}^{\rm HF} \quad (11)$$

where $E_{\rm pol}^{(1)}$ is the electrostatic energy of the monomers with the frozen electron distribution, $E_{\rm exch}^{(1)}$ is their first-order valence repulsion energy due to the Pauli exclusion principle, $E_{\rm ind}^{(2)}$ stands for the second-order energy gain coming from the induction interaction, $E_{\rm exch-ind}^{(2)}$ represents the repulsion change due to the electronic cloud deformation, $E_{\rm disp}^{(2)}$ is the second-order dispersion energy, and $E_{\rm exch-disp}^{(2)}$ stands for the second-order correction for a coupling between the exchange repulsion and the dispersion interaction. Detailed derivations of the various contributions are available in references 27, 42, and 60. A review of the latest developments in SAPT and its applications can be found in the review of van der Avoird in this issue.

While the choice of basis set is mainly dependent on the nature of the problem and the available computational resources, it is our observation that in the case of calculations involving π-systems, the chosen basis function should be able to reproduce the multipole moments and polarizabilities of the monomers and to recover large portions of the dispersion energy. While different groups have varying approaches to this choice of basis set, we believe that diffuse functions should be included in the basis set to obtain relatively reasonable results. In the past, Hobza and co-workers have shown that use of the 6-31+G* basis set leads to fairly accurate values of polarizability and the quadrupole moment of benzene.[61] Though a number of calculations reported herein have been carried out using the 6-31+G* basis set, the results obtained using the larger aug-cc-pVDZ, 6-311++G** and even larger basis sets are more reliable. It should, however, be noted that the use of the larger basis sets leads to a dramatic increase in the computational effort.

After the choice of a basis set, one is confronted with BSSE, which in most cases leads to an overestimation of the interaction energies. One of the widely used methods to correct for the BSSE is the counterpoise method.[62,63] Though a number of authors have provided both formal and numerical proof that counterpoise correction yields a pure interaction energy,[64−67] a number of recent papers have still raised doubts on the efficacy of this procedure in obtaining accurate interaction energies. This is particularly true when the size of the molecular cluster is large because one cannot employ very large basis sets to carry out these calculations. Some of the reasons for such doubts being raised are (i) the very large BSSEs encountered in such calculations, (ii) the large deviations exhibited by the BSSE-corrected interaction energies from the experimental estimates, and (iii) the computational effort involved in evaluating the BSSE corrections. More recently, some authors have claimed that the normal recipe of counterpoise correction of carrying out a single-point correction without further optimization does not find the correctly optimized structure.[68] Hence, they have advocated that geometry optimizations should be carried out using explicit BSSE corrections.[68] However, the computational effort associated with such methods is quite substantial, and hence, they are suitable for very small systems. Moreover, these optimizations lead to worse results in cases where the basis set incompletion error (BSIE) is substantial.

While, in principle, the errors in the interaction energy resulting from both BSSE and BSIE are negligible at the basis set limit, such calculations are computationally feasible only for very small systems, especially when electron correlation has to be explicitly included. Therefore, one is forced to use medium-sized basis sets to carry out these calculations. Though the BSSE-corrected interaction energies in such cases are theoretically accurate, they show large deviations from the experimental estimates. Efforts to explain this deviation have included those of Davidson and Chakravorty, who observe that with medium-sized basis sets, the counterpoise correction is able to provide a reasonable estimate of the intermolecular correlation repulsion effect but a large percentage of the corresponding intermolecular attractive correlation energy is not recovered.[69,70] On

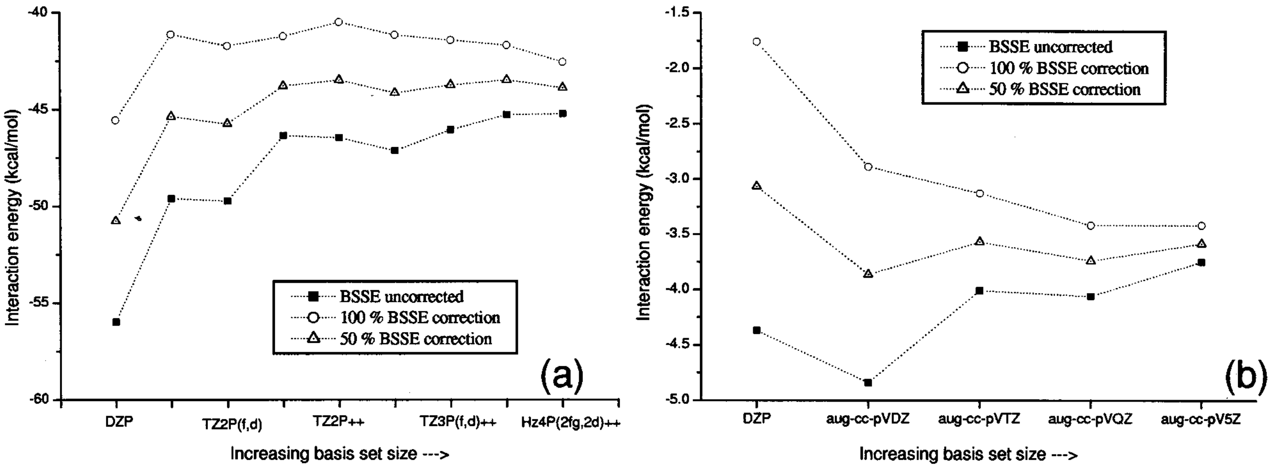


Figure 2. Comparison of different percentages of BSSE correction on (a) the water hexamer (ref 76) and (b) the Bz−H_2O complex (ref 77).

the other hand, Gutowski et al. asserted that the deviation arises from a poor choice of the basis set rather than from the counterpoise correction.[71] A more detailed and elaborate description of BSSE, the methods to correct it, and its effect on various molecular properties can be found in the reviews of van Duijneveldt and co-workers.[72,73]

Given this background, we found it useful to employ a 50% BSSE correction when comparing the theoretically evaluated quantities such as interaction energies, enthalpies, and free energies with the experimentally determined ones.[74−76] It should be clearly mentioned that the 50% BSSE correction cannot be theoretically justified, and as a result, many authors have advocated against its use. However, in the particular case of calculations of large molecular complexes with moderate basis sets, the method often yields good results because the ordinary BSSE tends to cancel the lack of dispersive interactions in small and moderate basis sets. Thus, in Figure 2, wherein the BSSE-uncorrected and -corrected interaction energies evaluated at the MP2 level are plotted for two different large systems (the ring form of the water hexamer[76] and the benzene−water (Bz−H_2O) complex)[77] with different basis sets, the 50% BSSE correction seems to yield decent interaction energies, especially with moderate basis sets. The 50% BSSE correction should, however, be used with caution. We advocate that various possibilities (carrying out calculations using different basis sets) of obtaining good interaction energies should be examined before using the 50% BSSE correction as a last resort. It is of interest to note that a similar strategy (mean of the uncorrected and BSSE-corrected interaction energies) was employed by Halkier et al. and Schütz et al. in their high-level theoretical studies of the water dimer to obtain accurate estimates of the interaction energy of the water dimer.[78,79]

A problem most frequently encountered in the field of molecular clusters is the comparison of the theoretically obtained values to the experimental data. Since in most cases the interaction energy is rarely obtained experimentally, one is forced to compare the values to the more easily obtained interaction enthalpies; i.e., in addition to the inclusion of zero-point vibrational energy (ZPVE), the temperature-dependent enthalpy terms should also be included. Thus, it becomes important to include the anharmonic contributions. However, this is easier said than done, because many practical problems are involved in an elaborate evaluation of the cubic and quartic force constants, which are necessary to evaluate the anharmonic corrections. Hence, success has been achieved for very small-sized clusters.[74,80] In the case of larger clusters, a compromise, therefore, has to be made between the level of accuracy needed and the available computational resources. In some cases, one can also carry out the anharmonic correction by considering only the highly anharmonic vibrational mode.

The role of atomic charges in monitoring the changes in the electrostatic profiles of the individual monomers as a result of cluster formation is well-known. Several theoretical schemes, which include those developed by Mulliken and Löwdin, have been employed to evaluate these charges. In recent years, the use of the natural bond orbital (NBO) analysis has been more widespread. Details of these scheme are available in a review by Reed and Weinhold.[81] An important highlight of this method is that unlike most other charge partitioning schemes, it is unaffected by the presence of diffuse functions in the basis set. A recent article describes the use of this method in the description of clusters.[82]

The theory of “atoms in molecules” (AIM), an innovative approach to probe the shifts in the electronic charge as a result of bond formation, has recently been applied to the investigation of weakly bound complexes.[83] While arguments have been extended against the use of this method on the basis that charge transfer does not explain the preferred orientations found in most intermolecular complexes, recent evidence obtained using both the AIMPAC and MORPHY programs[84,85] seems to suggest that in the case of some complexes it can be used to obtain significant insight into the nature of weakly bound complexes.[86−91]

Before we progress into a detailed discussion of the various complexes, we briefly highlight the terminology employed to describe the interaction energies in this review. To facilitate the comparison of the different terminologies used by various authors, the supermolecular BSSE-uncorrected and 100% BSSE-corrected interaction energies are represented as ΔE_e^N and ΔE_e^B. ΔE_e is the 50% BSSE-corrected interaction energy. The corresponding ZPVE-corrected interaction energies are denoted as ΔE_0^N, ΔE_0^B, and ΔE_0. The interaction energy obtained using SAPT is represented as E_{int}^{SAPT}. Since most of the large systems discussed in this review are beyond the limitations of the SAPT program, we have employed a simple scheme to obtain rough estimates of the correlation and electrostatic energies. Thus, the correlation energy (ΔE_{cor}) is defined as the difference of the MP2 (E_e (MP2)) and Hartree–Fock energies (E_e (HF)) at the MP2-optimized geometry. The electrostatic energy (ΔE_{es}) is the charge–charge interaction energy evaluated using the NBO charges. The NBO charges are evaluated with the electron densities obtained at the MP2 level. It should be noted that ΔE_{cor} and ΔE_{es} are very different from $E_{disp}^{(2)}$ and $E_{pol}^{(1)}$.

3. Weakly Bound π-Complexes

Dewar, in 1946, suggested that π-complexes could be formed with the π-system acting as a proton acceptor.[92] The earliest reported theoretical calculation of a "π hydrogen bond" (water–formaldehyde system) was carried out by Morokuma and coworkers in 1971.[93] However, the π-complexes formed through the involvement of polar π-bonds are not equilibrium structures, i.e., when the constraint of perpendicularity is removed, the complexes relax to a more stable dimer in which the hydrogen bonding occurs through a lone pair of electrons. On the other hand, the π-complexes formed by molecules possessing nonpolar π-bonds, such as ethene and benzene, are equilibrium structures and hence can be experimentally observed. Given this distinction, it is useful to explore the features of these π-complexes formed by nonpolar π-bonds.

It should be noted that though phenol, benzonitrile, and a large number of purines and pyrimidines are π-systems, their interactions with various countermolecules are mediated through the substituents constituting them rather than through the π-bonds.[94–118] Hence, these systems and their complexes are not discussed in this review.

The discussion of these complexes has been organized on the characteristics of their interaction energies. Thus, we initially focus our attention on the interaction of these π-systems with nonpolar systems, wherein the interaction energies are predominantly due to dispersive interactions. The nonpolar systems considered include, the rare gases, the dimers of oxygen and nitrogen, the dihalogens, and various hydrocarbons. Our discussion on hydrocarbons includes methane and a number of π-systems. Even though ammonia is a polar molecule, we discuss it alongwith methane because the complexes it forms with these π-systems are predominantly bound by dispersive interactions. Subsequently we concentrate on the characteristics of the interactions of these π-systems with various cations in a separate section. The high interaction energies of these π–cation complexes are, in general, dominated by electrostatic interactions. In the next section, we discuss the interaction of these π-systems with the water and methanol clusters. In these complexes, the interaction energies are controlled by a subtle interplay of dispersive, electrostatic, and cooperative interactions. The interactions of these π-systems with Lewis acids (the trihydrides and trihalides of boron and aluminum) are very interesting because the characteristics of the interaction energies are very dependent on the nature of the Lewis acid. Since hydrogen halides are also considered to be Lewis acids, the section on π–Lewis acid complexes also includes a discussion of the π–hydrogen halide complexes. In the discussion of the energetics of all these complexes, we highlight the crucial role of the repulsive interactions in dictating both the geometry and interaction energies.

3.1. Rare Gases

The fact that weakly bound complexes of π-systems with rare gases (RG) serve as prototype systems in the investigation of solvation at a microscopic level, particularly with respect to spectroscopic properties,[119] intermolecular vibrational redistribution, and vibrational predissociation, is well-known. Despite the abundance of both theoretical and experimental investigations on this subject,[9–12,120–160] the intermolecular interaction energies of the π–RG complexes are accurately known for only a few complexes. Theoretical characterization of these complexes is particularly challenging because of the predominance of dispersive forces in the interaction energy.[9] Thus, in addition to the use of large basis sets, calculations have to be carried out at very high levels of theory to obtain reasonably accurate results. Given the availability of a large number of accurate experimental results and the relative simplicity of the π–RG complexes, these theoretical calculations have been very useful in testing a number of novel methodologies and basis sets. Since the π–RG interaction has been the focus of a recent theoretical review,[9] we only highlight some recent theoretical calculations: (i) to provide an overview of the level of accuracy achieved in the theoretical description of these complexes, (ii) to elaborate on the efficacy of novel methodologies employed in the description of these complexes, (iii) to highlight the changes in the interaction energies resulting from differences in the nature of the π-system, nature of the rare gas, and the number of rare gas atoms complexing to the π-system. In the course of the review, the features of these π–RG complexes are compared with the other complexes.

Among π–RG complexes, the benzene–argon (Bz–Ar) system is one of the most widely studied complexes theoretically. In the most recent theoretical investigation of this complex, Koch et al. evaluated the interaction energies of both the ground (S_0) and excited (S_1) states using the coupled-cluster singles and doubles substitution with triples excitation (CCSD(T)) method.[147] The CCSD(T) calculations carried out on a system containing close to 464 basis functions yielded an interaction energy (ΔE_e^B) of −1.12 kcal/mol (−389 ± 2 cm^{-1}), which is in very good

Table 1. Interaction Energies (ΔE_e^B) (cm^{-1}) of the Ground State of the Benzene−Argon Complex. BSSE Uncorrected Values (ΔE_e^N) Are Given in Parantheses (Taken from ref 147)

basis set	DFT[a]	SCF	MP2	CCSD	CCSD(T)
aug-cc-pVDZ	226(177)	273(220)	−394(−560)	−194(−356)	−263(−437)
aug-cc-pVTZ	207(183)	279(251)	−493(−638)	−259(−391)	−356(−496)
aug-cc-pVQZ		281(274)	−522(−583)		−385[b]
$(-D_0)_{exp}$[c]					>−390

[a] DFT calculations using the B3LYP functional. [b] Estimated using the aug-cc-pVTZ values. [c] Evaluated from the D_0 upper limit of 340 (ref 152) and the corresponding vibrational ground-state energy (50 cm^{-1}) (ref 153).

agreement with the experimental value of −1.12 kcal/mol (−390 cm^{-1}).[152] More importantly, it was found for sufficiently large basis sets that the differences between the interaction energies obtained at the MP2 and CCSD(T) levels are quite systematic. Hence, based on the values obtained at the MP2/aug-cc-pVQZ level and the difference in the aug-cc-pVTZ CCSD(T)-MP2 numbers, the interaction energies at the CCSD(T)/aug-cc-pVQZ can be estimated to a high level of accuracy. A point which also emerges from these calculations is that the description of excited states can also be obtained to a high level of accuracy. Interestingly, the authors also compared the interaction energies obtained at different levels of theory for a number of basis sets. Though the best numbers for the interaction energy are obtained from a combination of large basis sets and high levels of theory, one also notices from Table 1 that the interaction energy (ΔE_e^B) obtained at the MP2/aug-cc-pVDZ level, −1.13 kcal/mol (−394 cm^{-1}), is very close to the experimentally obtained interaction energy of −1.12 kcal/mol (−390 cm^{-1}).[147] This seems to indicate that with a reasonably sized basis set the MP2 method is quite accurate. One can also see from Table 1 that the DFT method (B3LYP) does not even give reasonable estimates of the interaction energy.[147] Koch et al. elaborated on how the information obtained from the high-level theoretical calculations could be employed to develop a highly accuracte intermolecular potential-energy surface of the Bz−Ar system.[148] Apart from the theoretical calculations of Hobza et al.,[151] there are few high-level theoretical calculations of the complexes of benzene with other rare gas atoms. It can, however, be seen from Hobza's study that there is an increase in both the interaction energies and intermolecular distance as one progresses from Bz−He to Bz−Xe.[151]

What happens when fluorobenzene (FBz) or *p*-difluorobenzene (DFBz) form complexes with these rare gases? The calculations of Hobza and co-workers,[154] which were carried out using fairly small basis sets, seem to give some conflicting results with regard to the experimental observations of Parmenter and co-workers.[155] Thus, the theoretical numbers are unable to reproduce the gradual decrease in the intermolecular distance as one progresses from benzene to fluorobenzene and difluorobenzene.[154,155] The calculated interaction energies seem to indicate that the FBz−Ar complex is the most strongly bound, compared to either Bz−Ar or DFBz−Ar. This is particularly surprising when one takes into account the decreased π electron density of fluorobenzene. In this context, it is interesting to recapitulate the findings of Kuczkowski and co-workers.[146] On the basis of ab initio calculations of fluorobenzene, they concluded that the regions of highest electrostatic potential and, therefore, greatest polarizing forces are in the plane of the ring. Moreover, they also find that the dispersion forces are maximized at sites above the aromatic ring. Since the RG is placed directly over the aromatic ring in the FBz−RG and DFBz−RG complexes, dispersion effects are dominant contributors to the interaction energy.

The ideas put forward in a pair of papers on theoretical calculations of these π−RG complexes by the group of Kraka and Cremer on the Ar−oxazole and Ar−isoxazole complexes are very interesting.[149,150] Though the ab initio calculations reported therein were employed to supplement the findings obtained from the rotational spectrum of these complexes, the study involves an innovative use of the electron density to unravel the electronic factors determining the stability and the configuration of a van der Waals complex. Thus, an analysis of the Laplace concentration of the monomers helped detect regions of strong contraction of negative charge and small exchange repulsion. On the other hand, the difference in the electron density distribution of the complex reveals that the acting intermolecular forces increase or decrease the electron density. On the basis of the electron density profiles, the argon complexes of these aromatic molecules were distinguished between situations where the density at argon is either pulled toward the partner molecule (Ar−oxazole) or pushed toward the back of argon (Ar−Bz). Thus, in the case of Bz−Ar, the difference density distribution, which is a result of exchange repulsion and mutual charge polarization, showed that the destabilizing exchange repulsion effects would be smallest over the ring center while the dispersion effects would be larger over the carbon atoms. The observed geometry of the Bz−Ar complex, therefore, indicates that while a combination of dispersive and inductive effects stabilize the complex, the destabilizing exchange repulsion directs argon above the center of the ring to a position where the exchange repulsion is the weakest. In the case of Ar−oxazole, the difference electron density distribution maps are able to account for the preferred minimal energy geometry. Thus, in Figure 3 it can be seen that there is a hole in the electron distribution above the oxygen atom (Figure 3d). The presence of this hole, inferred from the diminished Laplacian concentration over the oxygen atom of oxazole, leads to a polarization of the negative charge of the argon in the direction of the oxygen atom. As a result, the exchange repulsion effects are smaller in the region between argon and oxygen and the buildup of nega-

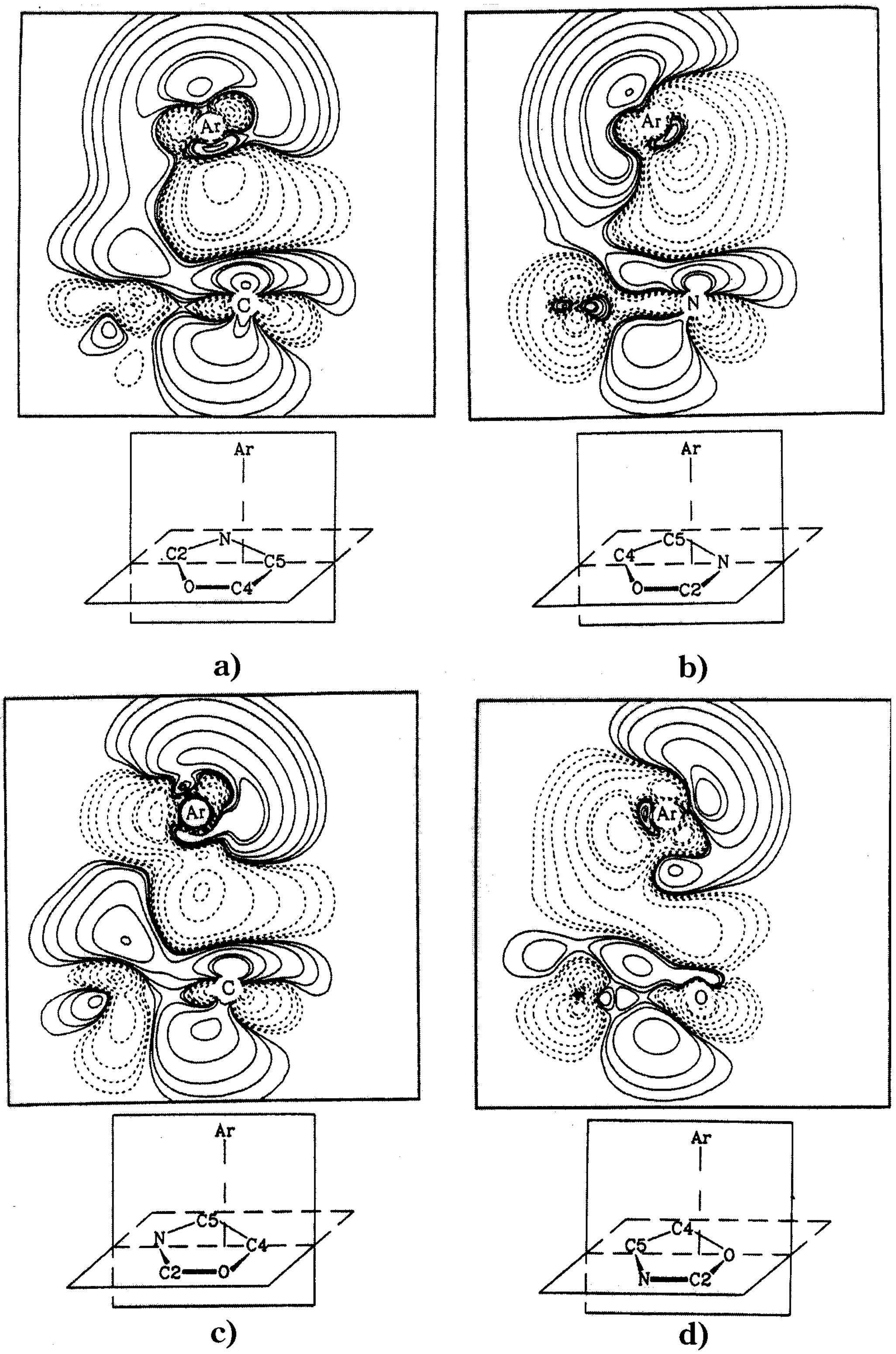


Figure 3. Contour line diagram of the MP2 difference electron density distribution of oxazole−argon. $\Delta\rho(r) = [\rho(\text{oxazole–argon}) - \rho(\text{oxazole})^{\text{DCBS}} - \tilde{n}\,(\text{argon})^{\text{DCBS}}]$, using the 6-31G(+sd,+sp) basis for oxazole and the [7s4p2d1f] basis for argon. A dimer-centered basis set (DCBS) was used in the calculations. The reference plane is schematically indicated in the figure. Contour lines range from 2×10^{-6} to 2×10^{-1} [e/bohr^3]. Solid lines correspond to an increase of electron density upon complex formation and dashed lines to a decrease. (Reprinted with permission from ref 149. Copyright 1995 American Chemical Society.)

tive charge in the region between argon and oxygen atom is favored (Figure 3a−d). It can also be seen from Figure 3a−c that such a buildup is not favored between argon and the other atoms. As a result of the suggestions of one of the referees, we carried out SAPT calculations of an angular dependence of the interaction energy terms of the Bz−Ar system.[161] These calculations indicate that the exchange−repulsion is minimal at the top of the ring. As the Ar atom comes closer to the benzene carbon atom, the increase in the dispersion energy is accompanied by a larger increase in the exchange−repulsion energy, which is

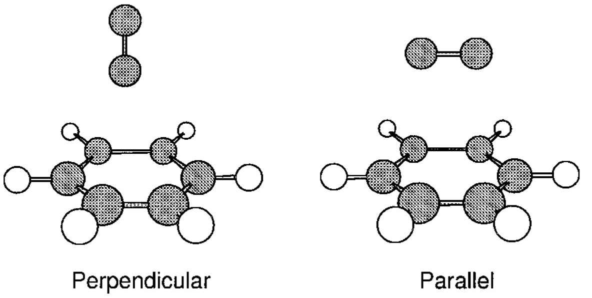


Figure 4. Perpendicular and parallel orientations of the Bz−X (X = N_2, O_2, CO) complexes.

in agreement with the simplistic conclusions of Kraka et al.[149,150]

Using these ideas on the interplay of dispersive and repulsive interactions in dictating the geometry of the rare-gas atom, Wilson et al. were able to explain the position of the neon atom in the FBz−Ne complex.[146] The Ar−thiopene complex is another interesting example which highlights the crucial role of repulsive interactions in dictating the geometry of these complexes.[156] Despite the greater electronegativity of the sulfur compared to the carbon atom, the larger size of the electronic cloud of sulfur precludes the closer approach of argon to sulfur.

A recent study on the interaction of argon with anthracene also merits mention because the authors, using a very simple potential consisting of dispersive, repulsive, and polarization terms, were able to reproduce the experimental ionization energies and explain nearly all the exhibited spectral features.[137]

What emerges from the theoretical studies of the complexes of these rare gases with different π-systems is that the repulsive interaction plays a vital role in dictating the geometry of these weakly bound π-complexes. Second, the attractive interactions which bind the rare gases to the π-system are predominantly dispersive in nature. Hence, the basis set size and the level of correlation employed play a vital role in the determination of accurate interaction energies.

3.2. Nonpolar Diatomic Molecules

Interest in understanding the intricacies of gas/surface interaction chemistry has led to theoretical investigations of the interactions of various π-systems (notably benzene) with O_2, N_2, and CO.[9,13] In these complexes the ligand can have two possible orientations: parallel or perpendicular to the plane of the π-system (Figure 4).[9,162−167] It has been observed that in both the Bz−N_2 and Bz−O_2 complexes, the parallel orientation is more favored over the perpendicular orientation. In the case of the Bz−CO complex, the carbon monoxide is tilted away from the parallel arrangement, with the carbon end being closer to the benzene plane.[166] The calculated interaction energies (ΔE_e^B) (Figure 5) indicate that N_2 is more strongly bound to benzene than either O_2 or CO.[163] Expectedly, dispersive interactions dominate the interaction energies of these complexes. There have been attempts to obtain the interaction energies of these complexes using DFT methods, but the accuracy of these calculated interaction energies is very much dependent on the kind of DFT functionals and basis sets employed.[164]

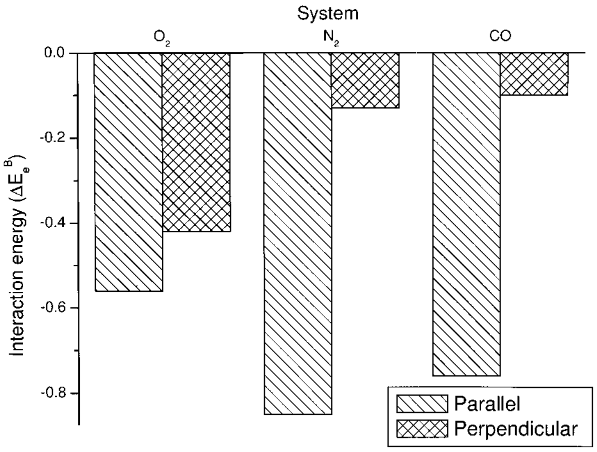


Figure 5. Comparison of the interaction energies obtained for the Bz−X (X = N_2, O_2, CO) complexes at the MP2/6-31G** level. Values obtained from ref 163.

Table 2. Experimental Values for the Interaction Enthalpies (ΔH) and D_0 for Aromatic + O_2 Complex Formation (Taken from ref 168; the original table was in units of kJ/mol)

aromatic molecule	ΔH (kcal/mol)	D_0 (kcal/mol)	ref
benzene	−1.03 ± 0.24	1.72	169
	−1.89	2.58	170
	−0.96 ± 0.36	1.65	171
toluene	+0.26 ± 0.22	0.43	168
fluorobenzene	−1.29 ± 0.50	1.98	168

Recently there have been some accurate experimental determinations of the enthalpies of reaction of some of these complexes.[168−171] Thus, the experimental interaction energies (Table 2) of the Bz−O_2, Tol−O_2, FBz−O_2, and C_6F_6 −O_2 complexes yield some unexpected results. On the basis of the knowledge that the interaction energies of these complexes are dominated by dispersive interactions, what one might expect is that the Tol−O_2 complex would exhibit the highest interaction energy and the FBz−O_2 complex the lowest. However, the experimental results indicate the contrary. It would be interesting to theoretically investigate the reasons for the anomalous behavior of these O_2 complexes.

The complexes of the dihalogens with various π-systems have triggered much interest in the context of prereactive complexes. Prereactive complexes (or intermediates) describe complexes formed prior to a chemical reaction or significant charge transfer. Recently, Legon reviewed both the experimental and theoretical advances in the description of these complexes.[172] In the context of this review, we think it would be useful to discuss the characteristics of Bz−I_2, which is one of the most well-studied π−dihalogen complexes. In a recent theoretical study of this complex, the atom−atom potential parameters obtained from a detailed ab initio investigation were employed in a molecular dynamics simulation of the dissociation of iodine in benzene clusters.[173] The ab initio study on eight different conformers of the Bz−I_2 complex indicates that in the minimal energy geometries, the I_2 axis is perpendicularly oriented to the plane of the benzene ring and pointed toward either the center of the C−C bond or a carbon atom of benzene. These observations indicate that minimal energy geometries of the complexes of these dihalogens with benzene are very different from what is observed in the case of Bz−N_2, Bz−O_2, and Bz−CO. On the basis of an empirical decomposition of the calculated interaction energy, the stability of the Bz−I_2 complex was attributed to be predominantly due to a combination of dispersive and repulsive interactions. However, electrostatic interactions between I_2 and benzene were found to be important in governing the structure and dynamics of the benzene solvent cage around iodine.

Thus, the theoretical studies of O_2, N_2, CO, and these dihalogens with various π-systems indicate that a subtle interplay of dispersive and repulsive interactions dictate the geometries and interaction energies. One also notices that in condensed phases of these systems, electrostatic interactions also become important. In the next section, we examine the intricacies of $\pi-\pi$ interactions.

3.3 Nonpolar Alkane Derivatives and Weakly Polar Ammonia

Unlike the complexes of π-systems with rare gases, diatomic molecules, or other π-systems, relatively few studies exist on their complexes with nonpolar spherical molecules such as methane. This scarcity has more to do with the relatively weak but much more complex interactions prevalent in these complexes. The π-complex with methane also heralds the emergence of the π−H interaction which gradually increases in strength as one progresses from methane to hydrogen fluoride. This increase in the strength of the π−H interaction, apart from contributing to the increased interaction energies of these complexes, also leads to a substantial increase in the anisotropy of the intermolecular potential. Additionally, one also notices a substantial increase in the electrostatic contributions alongwith a gradual decrease in the dispersive contributions as one progresses from methane to hydrogen fluoride (HF). While we discuss the interactions of these π-systems with HF in the section dealing with Lewis acids, their interactions with the water and methanol clusters are discussed separately.

3.3.1. Literature Overview

One of the earliest detailed experimental and theoretical investigations of methane complexes has been the study of Bernstein and co-workers on the complexes of benzene and toluene with various alkanes.[174−177] Using an atom−atom intermolecular potential, the interaction energies of these complexes were also evaluated. Expectedly, the alkanes are more strongly bound to toluene than to benzene. Subsequent investigations by the Bernstein group were devoted to the complexes of various alkanes, ammonia (NH_3), and water with heterocyclic π-systems such as pyrazine, pyrimidine, etc.[178−181] In the case of pyrimidine−NH_3, their calculations seemed to suggest that the ammonia hydrogens are oriented more toward the π-system of pyrimidine than to the nitrogen. They also evaluated the van der Waals mode energies of Bz−CH_4, Bz−CD_4, and Bz−CF_4 using time-of-flight mass spectroscopy (TOFMS) and theoretical calculations using empirical potentials and obtained an excellent agreement.[182] Similar studies were carried out by them on complexes of methane and ammonia with toluene and aniline.[183−186] The study on the complexes of the benzyl radical merits mention because it showed that the effects of solvation on reactive intermediates could be elucidated through a combination of experimental and theoretical studies.[187]

The first ab initio studies of π-systems complexed with ammonia were carried out by Cheney et al. on Bz−NH_3 at the MP2/6-31G*//HF/3-21G(*) level.[188] However, the calculated interaction energy was underestimated owing to the optimization being carried out at the Hartree−Fock level. Bredas et al. carried out similar calculations on the interactions of methane, ammonia, and formic acid with benzene.[189] Interestingly, the calculations on the Bz−NH_3 complex lead to a great deal of uncertainity on whether ammonia behaves as a proton donor or acceptor.[190] The issue was finally resolved by the microwave study of the Bz−NH_3 complex by Rodham et al.[191] The experimental spectra alongwith the high-level ab initio calculations indicated that ammonia is the proton donor and benzene is the proton acceptor. Additionally, the study also indicated that the Bz−NH_3 interaction is weaker than the corresponding Bz−H_2O interaction. There have been a couple of high-level ab initio calculations on the structures and interaction energies of complexes of methane with benzene, ethene (Et), and ethyne (Ey) in the recent past.[192,193] The very recent investigation of Et−CH_4 and Ey−CH_4 includes calculations carried out at the CCSD(T) level.[193] An interesting offshoot of the interaction of benzene with methane was highlighted by Hobza and co-workers.[194] Thus, the blue shift associated with the stretching frequency of the proton donor in these complexes was termed to be the signature of an anti-hydrogen bond.[195] The anti-hydrogen bond has recently been rechristened as improper blue shifting of the hydrogen bond.[1] More details on the features of this hydrogen bond can be obtained from the review of Hobza in this issue. The interaction of *o*-, *m*-, and *p*-difluorobenzene with ammonia has been the focus of an experimental investigation by Hu et al.[196] Their study also includes some theoretical calculations carried out at the MP2/6-31G** level.

3.3.2. Theoretical Studies

An ab initio study of the Bz−NH_3 system, which included full geometry optimization at the MP2/6-31G** level, was carried out by Rodham et al.[191] The calculated equilibrium structure with a R_{CM-CM} of 3.43 Å is lower than the experimentally obtained R_{CM-CM} of 3.590 ± 0.005 Å, where CM denotes the center-of-mass of each monomer. More importantly, the theoretical data indicate that in the global minima, only one of the hydrogens of ammonia is directed toward the benzene π cloud, which is in agreement with the experimental predictions. The geometry in which two hydrogens are directed toward the benzene π cloud is only about 0.1 kcal/mol higher in energy than the global minimum. The interaction energy evaluated at the global minimum of the Bz−NH_3 complex indicates that it is weaker than the Bz−H_2O interaction. A recent calculation at the MP2/6-31G**level on *p*-difluorobenzene with ammonia indicates that the nitrogen lies over the π-system and the intermolecular R_{CM-CM} distance is 3.53 Å, which is only 0.10 Å larger than what is observed in the Bz−NH_3 interaction.[195]

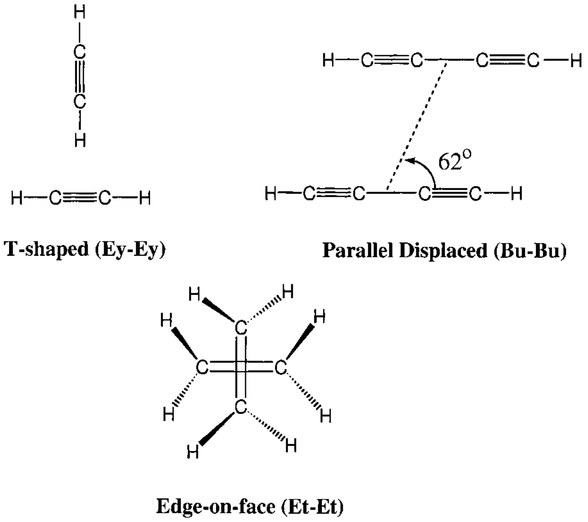
Sakaki and co-workers evaluated the interaction energy of different conformers of the Bz−CH_4 complex at the MP2 level.[192] Though they fixed the geometries of both benzene and methane to their optimized structures in the monomeric state, the scans were carried out with respect to the internuclear distance. Thus, using the MIDI-4 basis set, they obtained an interaction energy (ΔE_e^B) of −0.43 kcal/mol for the lowest energy conformer at the MP4(SDQ) level. In a recent paper, Hobza and co-workers reported an interaction energy (ΔE_e^B) of −0.3 kcal/mol at the MP2/6-31G** level. The focus of their work is, however, not on the evaluation of the interaction energies but on the vibrational frequencies.[194]

Apart from the recent theoretical investigation of the ammonia complex of aniline,[197] wherein the ammonia molecule interacts with the aniline nitrogem, no high-level theoretical calculations exist on the complexes of ammonia with other π-systems. The interaction of methane with ethene was investigated using very high-level theoretical calculations.[193] On the basis of the CCSD(T) and MP2 values, the interaction energy (ΔE_e^B) of the Et−CH_4 complex was estimated to be about −0.49 kcal/mol. Given the low interaction energies and the flat intermolecular potential-energy surface, the energetic differences as a result of changes in the orientation of the methyl hydrogens are very small.

3.4. Complexes with Other π-Systems

Much attention has recently been focused on the interactions between π-systems, especially the aromatic π-systems,[7,9,10,198−226] because of their relevance in the stacking of base pairs in DNA,[227,228] protein structure,[231−234] molecular recognition,[229,230] and properties in condensed phases.[235,236] An equal amount of literature is also available on the interactions prevailing between the olefinic π-systems.[237−252] In this brief account on π−π interactions, apart from highlighting the new theoretical insights, we also compare the olefinic π−π and aromatic π−π interactions.

The simplest system which can exhibit a π−π interaction is the ethyne dimer.[237−240] Karpfen very recently carried out a high-level theoretical study of this system.[240] At the MP2/aug-cc-pVTZ level, the interaction energies (ΔE_0^B) indicate that the T-shaped C_{2v} conformer (Figure 6) exhibiting a π-type of H-bond is only 0.09 kcal/mol more stable than a parallel displaced C_{2h} conformer. On the other hand, the D_{2d} conformer is about 0.8 kcal/mol less stable than the minimum C_{2v} structure. The calculations at higher levels of correlation including those carried out at the CCSD(T) level indicated that these relative differences in the interaction energies are intact. Another highlight of this study was that both Hartree−Fock and DFT calculations are inadequate in describing either the geometry or the interaction energy of this system. What was more interesting in this study was the results obtained at the same level of theory on the 1,3-butadiyne dimer. It was shown that the parallel displaced C_{2h} conformer (Figure 6) becomes more stable than the other possible conformer. Thus, an increase in the chain length leads to a dramatic change in the conformational preference. Similar results were obtained for the cyanoethyne dimer by the same author.[242.243] These results indicate the crucial importance of dispersive interactions in determining the conformations exhibited by these system.


T-shaped (Ey-Ey)

Parallel Displaced (Bu-Bu)

Edge-on-face (Et-Et)

Figure 6. Minimum energy structures of the ethyne (Ey−Ey), 1,3-butadiyne (Bu−Bu), and ethene (Et−Et) dimers.

It is interesting to observe the change in conformational preference of this π−π interaction when the π-system is a double bond. Early ab initio calculations by Tsuzuki et al. on the ethene dimer indicated that a D_{2d} conformer (Figure 6) is the most stable among all the other possible structures.[245] This structure, which is held by four equivalent hydrogen bonds (quadruple hydrogen bond), was confirmed by the rotationally resolved near-infrared spectroscopic study of Miller and co-workers.[250] It is also consistent with the results obtained from the matrix isolation studies of Rytter and Gruen.[252] In a recent theoretical study, Tsuzuki et al. evaluated the interaction energy of this system at the CCSD(T)/aug(d,p)-6-311G** level.[244] The interaction energy (ΔE_e^B) of this system at this level of calculation was found to be −1.15 kcal/mol.[244] The interaction energies of the Bz−Ey and Bz−Et complexes have been reported very recently.[221] In both these cases, the ethyne and ethene hydrogens are pointed toward the benzene π cloud. Given the acidic nature of the ethyne hydrogen, the interaction energy (estimated CCSD(T) interaction energies (ΔE_e^B) at the basis set limit) of the Bz−Ey complex (−2.83 kcal/mol) is larger than that of the Bz−Et complex (−2.06 kcal/mol).[221] On the basis of an ab initio study of the Ey−Ey, Et−Et, Et−Ey, Bz−Et, Bz−Ey, and Bz−Bz complexes at the MP2/6-31+G-

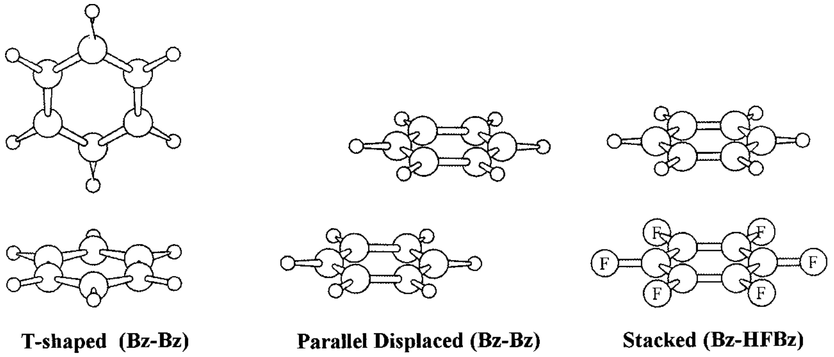


Figure 7. Minimum energy structures exhibited by the benzene dimer (Bz−Bz), benzene−hexafluoro−benzene complex (Bz−HF−Bz).

(2d,2p) level, Novoa and Mota correlated the strength of the C−H···π interaction to the hybridization of the C−H carbon atom and the delocalization of the π-system.[226] Thus, the interaction energy decreases with the hybridization of the C atom in the order C(sp) > C(aromatic) > C(sp^2) > C(sp^3) while progressing from the π-delocalized to π-localized systems.

As one progresses to the benzene dimer, one observes that both the parallel displaced and T-shaped conformers (Figure 7) are nearly isoenergetic.[194,201,202] While more details of the T-shaped conformer and its characteristics can be obtained from the contribution of Hobza in this issue, what is of interest to us are the geometries exhibited by the lowest energy structures of these complexes displaying π−π interactions. Thus, a parallel displaced structure is most stable in the case of both the 1,3-butadiyne and benzene dimers. On the other hand, the highly acidic nature of the ethyne hydrogen leads to the stabilization of the T-shaped conformer in the ethyne dimer. The ethene dimer, on the other hand, displays a structure very different from both the ethyne and benzene dimers. Thus, there is a subtle interplay of repulsive, electrostatic, and dispersive forces in governing the anisotropy of the total interaction energy. Similar conclusions were made in a recent theoretical investigation of the pyrrole dimer using SAPT, wherein it was shown that a large increase in electrostatic energy in most cases is compensated by an equally large increase of the exchange energy.[211] The interaction energies of some of the conformers of the naphthalene dimer have recently been evaluated.[220−222] The results indicate that the interaction energies of the different conformers of the naphthalene dimer are larger than the corresponding conformers of the benzene dimer.

How does the presence of substituents on the aromatic ring influence this π−π interaction? We begin a discussion of this subject by considering the interaction of benzene with hexafluorobenzene (HFBz). In hexafluorobenzene, the quadrupole moment of benzene is reversed because of the presence of the electron-withdrawing fluorine atoms.[253−255] Thus, a parallel-stacked geometry (Figure 7) is observed in the case of the Bz−HFBz complex.[204−208] It would be widely expected that the interaction energy of this complex would be dominated by electrostatic interactions with the electron-rich π cloud of benzene interacting with the electron-deficient π cloud of hexafluorobenzene. Surprisingly the Hartree−Fock calculations carried out on the MP2 geometry lead to a repulsive interaction.[208] A similar situation is also observed in the case of the parallel-stacked benzene dimer.[209] Though these results lead to the conclusion that dispersion is very important in obtaining an accurate estimate of the interaction energy, it should also be noted that the significant electrostatic interaction in the Bz−HFBz complex would be compensated by the equally large exchange−repulsion energy. Thus, the presence of an electron-withdrawing substituent has only a marginal effect on the π−π interaction. It would be, however, shown in the case of the interaction of water clusters with these π-systems that the presence of an electron-withdrawing substituent on the aromatic ring has a dramatic effect on the conformations exhibited by the π-complexes.

What happens when an electron-donating substituent is present? Kollman and co-workers carried out an investigation on the toluene dimer at the MP2/6-31+G(2d,2p) level of theory to rationalize the conformational preferences of phenyl side chains in protein secondary structures. They found that the parallel-stacked structure (with the methyl groups on the opposite sides) is the most stable conformer.[215] Recently, Felker and co-workers in the course of a rotational coherence spectroscopic (RCS) study on a number of aromatic−aromatic complexes carried out calculations using a simple atom−atom pair potential[256] on perylene−benzene, perylene−toluene, fluorene−benzene, and fluorene−toluene complexes.[217] Their calculations on the perylene complexes seemed to indicate that the experimental rotational constants are consistent with a centrally bound parallel stacked structure, with the monomer planes being separated by an intermolecular distance of 3.5−4.3 Å. Interestingly, Topp and co-workers obtained similar results on the perylene complexes with *p*-chlorobenzene, *p*-difluorobenzene, and hexafluorobenzene.[219] On the other hand, the structures of the fluorene compelexes are consistent with parallel displaced structures.[217]

It is of interest to note that the information gleaned from these theoretical investigations of the π−π interactions could be used to explain the arrangement of layers in crystals[257,258] and the conformational behavior exhibited by a number of intramolecular systems possessing aromatic rings.[259−266]

Table 3. Calculated M^+−Benzene Centroid Distances (Å) and Enthalpies (kcal/mol) of Different Benzene−Metal Cation Complexes (Taken from ref 274)

	RHF/6-311G*		MP2/6-311+G*		SVWN/TZ94p[a]		
M	$M^+-\Phi$	$-\Delta H_{298}$[b]	$M^+-\Phi$	$-\Delta H_{298}$[b]	M^+ Φ	$-\Delta H_{298}$[b]	$-\Delta H_{\mathrm{exp}}$
Li^+	1.892	37.0	1.865	34.3	1.805	38.1	37.9[c]
Na^+	2.475	22.7	2.426	21.0	2.301	26.4	28.0[d]
K^+	2.992	14.2	2.894	16.7	2.769	18.3	18.3[e]
Rb^+	3.286	11.6	3.165	13.9	3.046[f]	15.7[f]	
Cs^+	3.605	9.6	3.414	12.1	3.308[f]	13.6[f]	

[a] SVWN (Slater exchange and Vosko−Wilk−Nusair correlation). [b] The interaction enthalpies were calculated at 298.15 K using the BSSE- and ZPVE-corrected interaction energies. [c] The experimental enthalpy at 298.15 K for Li^+ is estimated from the thermodynamic data given in ref 283. [d] The experimental enthalpy at 610 K for Na^+ is from ref 284. [e] The experimental enthalpy at 500 K for K^+ is from ref 285. [f] These calculations were carried out using the Hay−Wadt effective core potentials and the TZ94p basis sets.

4. Cation−π-Complexes

Given the importance of cation−π interactions in diverse fields ranging from molecular recognition to neurobiology,[267,268] theoretical investigations have been very useful in obtaining a clear understanding of the same. An elaborate account of the importance of cation−π interactions in biological systems is available in the review of Ma and Dougherty.[269] In the present account,[270−279] we focus our attention on the changes in the characteristics of the cation−π interaction energy as a result of changes in the π-system (susbstituent effects) and cation (metal vs organic) are examined. We also elaborate on how the presence of a counterion influences the cation−π interaction.[280,281] It should be noted that in the case of transition-metal cations, the presence of d orbitals dramatically alters the nature of the interaction. This is illustrated in a recent investigation of the interaction of benzene with the cations and anions of rhodium and niobium. It was shown that the charge on the metal has little affect on the nature of the interaction with benzene.[282]

Recently, Nicholas et al. investigated the interaction of the alkali cations (Li^+, Na^+, K^+, Rb^+, Cs^+) with benzene and anisole using ab initio calculations.[274,275] In Table 3, the interaction enthalpies of the benzene complexes calculated at different levels of theory are listed. The values indicate that one can obtain fairly accurate estimates of the experimental enthalpies at the Hartree−Fock level itself.[283−285] This clearly illustrates the predominance of electrostatic interactions in the binding of these alkali cations to benzene. However, dispersive interactions become more important as the size of the metal cation increases. This is evident from the significant differences in the HF and MP2 calculated interaction enthalpies of the Rb^+ and Cs^+ complexes. It can also be seen from Table 3 that DFT methods (SVWN/TZ94p) provide fairly accurate estimates of the interaction enthalpies. The quantum chemical investigations of the interaction of various alkali-metal ions with anisole (methoxy benzene) indicate that the metal cation could bind either to the oxygen atom or the π cloud of the aromatic ring.[275] The nearly similar interaction enthalpies (Table 4) obtained for the binding of the metal cations to both the oxygen and the aromatic ring of anisole illustrates the difficulty in predicting the exact structure of the anisole−M^+ complexes. A notable feature of theoretical studies of these alkali cation−π-complexes is that the interaction energy decreases significantly as the size of the metal cation increases.

Table 4. Distances (Å) and Interaction Enthalpies (kcal/mol) Calculated at the MP2/6-311+G* Level for the Anisole−Metal Cation Complexes (Taken from ref 275)

	oxygen[a]		ring[b]	
M	M^+-O	$-\Delta H_{298}$[c]	M^+-C[d]	$-\Delta H_{298}$[c]
Li^+	1.822	37.7	2.333	38.1
Na^+	2.244	25.2	2.793	23.6
K^+	2.617	19.4	3.196	18.3
Rb^+	2.868	16.4	3.440	15.4
Cs^+	3.104	14.3	3.703	13.6

[a] Metal cation is bound to the anisole oxygen. [b] Metal cation is bound to the ring. [c] The interaction enthalpies were calculated at 298.15 K using the 100% BSSE- and ZPVE-corrected interaction energies. [d] Metal cation−ring carbon distances.

Though the interactions of the alkali cations with the simpler π-systems such as benzene are predominantly electrostatic, recent results of Cubero et al. seem to indicate that other effects such as the size of the aromatic ring (five- or six-membered or polycyclic rings) significantly influence the interaction energies.[286] These effects become important particularly when the electron density of the π aromatic cloud is diminished due to the presence of substituents on the ring. An increase in the positive charge of the metal cations significantly increases the interaction energy.[287,288] The prediction of the site of binding of the metal cation is particularly tricky in polycyclic aromatic π-systems. Thus, in the case of of Na^+−indole, it was found that the binding of Na^+ to the benzene π cloud is favored by ~4 kcal/mol over that of the pyrrole π cloud.[288] Similar conclusions were arrived at from an examination of the electrostatic potential surface of indole.[289] However, a recent experimental study by Gokel and collaborators[290] seems to suggest that the metal cations Na^+ or K^+ are located over the pyrrole ring rather than on the benzene ring. It would be of interest to theoretically explain this experimental observation.

Though there have been a number of theoretical studies of the interactions of various electrophiles (like CH_3^+, NO_2^+) with benzene, few have examined the characteristics of the binding of these organic cations. Thus, it would be of interest to compare the characteristics of the interactions of these organic cations with the metal cations. In the Bz−CH_3^+

Table 5. Intermolecular Distances (Å) and Interaction Energies (ΔE_e) (kcal/mol) for the Complexation of Benzene with $(Me)_nH_{(4-n)}N^+$

	6-31G*										6-311+G**	
	0		1		2		3		4		0	4
$n\rightarrow$	HF	MP2	HF	MP2	HF	MP2	HF	MP2	HF	MP2	MP2	MP2
$\delta R_{N-H\pi}$[a]	0.0019	0.0051	0.0028	0.0042	0.0010	0.0037	0.0024	0.0037	−0.0004	0.0004	0.0056	0.0005
δR_{N-Hn}[a]	−0.0030	−0.0031	−0.0005	−0.0042					0.0002	0.0004	−0.0029	0.0005
δR_{N-C}[a]			−0.0011	−0.0111	−0.0080	−0.0095	−0.0080	−0.0062	−0.0001	−0.0007		−0.0011
$-\Delta E_e^B$[b]	14.49	16.71	12.75	15.91	11.52	15.00	9.63	13.42	5.74	8.35	16.88	8.67
$-\Delta E_e$[b]	14.95	17.91	13.29	17.20	12.15	16.61	10.42	15.78	6.27	9.78	17.93	10.20

[a] $\delta R_{N-H\pi}$, δR_{N-Hn}, δR_{N-C} are the bond length increments compared to the monomeric state. The H_π hydrogen interacts with the benzene π cloud, while the H_n hydrogen does not. $\delta R_{C-H\pi}$ and δR_{C-Hn} for $n = 4$. See also Figure 9. Taken from ref 298. [b] ΔE_e^B and ΔE_e are the 100% and 50% BSSE-corrected interaction energies, respectively.

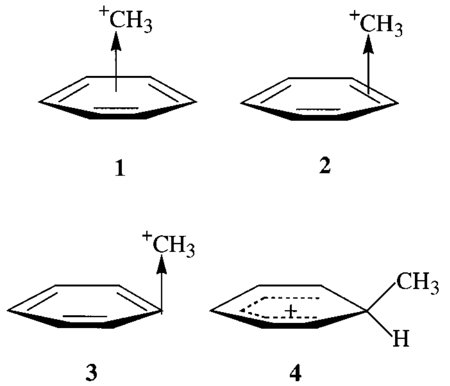


Figure 8. Conformers for the complex of methyl cation and benzene, three types of π-complex, **1**(η^6), **2**(η^2), and **3**(η^1), and one type of σ complex, **4**. (Reprinted with permission from ref 291. Copyright 1998 American Chemical Society.)

complex,[291,292] the conformer possesing a C_{3v} symmetry (the methyl cation is located on the benzene C_6 axis) is a transition state. The MP2/6-311+G* interaction energy of this C_{3v} conformer is 25.2 kcal/mol, while the interaction energy (ΔE_e^N) of the corresponding C_s conformer is 83.1 kcal/mol (Figure 8). The interaction energy of this C_s conformer, which is a stable minimum, is governed by charge transfer from the benzene π orbital to the empty p_z orbital of the methyl carbon. A similar type of interaction prevails in the Bz−SiH_3^+ complex.[293−295] Unlike what is observed in the case of metal cations, one observes that the geometry of the Bz−XH_3^+ complex is very different.

The interaction of the ammonium cation with benzene is an interesting example of a cation−π interaction dominated by dispersive forces. Three different conformers, each of them differing by the number of hydrogen atoms directed toward the benzene ring, are feasible for this interaction. Calculations by Meot-Ner et al. at the HF/3-21G level indicated that the conformer in which three hydrogens are directed toward the benzene ring is the least stable.[296] Calculations by Kim and co-workers,[297,298] at the MP2/6-31G* level, indicated that a single hydrogen atom pointing toward the benzene ring is the least stable conformer. In the lowest energy structure of the Bz−NH_4^+ complex, the nitrogen atom is located over the C_6 axis and two hydrogen atoms point toward the benzene ring, as shown in Figure 9. Unlike the interaction of metal cations with benzene, there are significant differences in the geometries and interaction energies of the Bz−$(Me)_nH_{(4-n)}N^+$ complexes obtained at the Hartree−Fock and MP2 levels. Conventional wisdom suggests that if the origin of the interaction is purely due to electrostatic or induction forces, calculations at the MP2 level should not lead to a significant increase in the interaction energy. However, one observes the contrary with the interaction energies (ΔE_e) of the Bz−NH_4^+ and Bz−$N(CH_3)_4^+$ complexes at the MP2/6-311+G* level being −18 and −10 kcal/mol (Table 5). A quantitative analysis of the interaction energies of the complexes of the ammonium and tetramethylammonium cations with benzene and water (Table 6) reveals that in the −NH_4^+ and −$N(CH_3)_4^+$ complexes, the charge−dipole interaction has a significant contribution to the interaction energy. However, in the Bz−NH_4^+ and Bz−$N(CH_3)_4^+$ complexes, the charge−quadrupole, charge−polarizability, and dispersive energies become important. An analysis of the lowest unoccupied molecular orbital (LUMO) of the Bz−$N(CH_3)_4^+$ complex at the MP2/6-311+G* level indicates that there is a significant gain in the electron correlation energy due to the interaction between the π electrons of benzene and the orbitals of the tetramethylammonium cation. This indicates that electron correlation involving the π−σ_{C-H}* in-

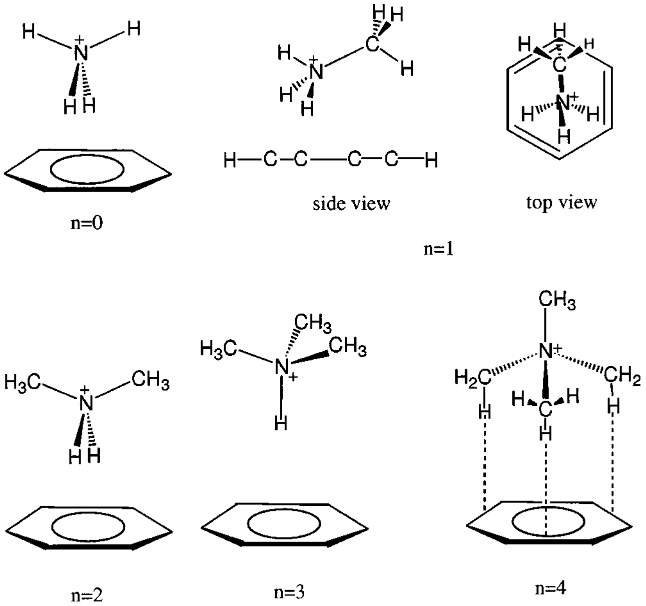


Figure 9. Minimum energy structures for the benzene complexes with $(Me)_nH_{(4-n)}N^+$. (Reprinted with permission from ref 298. Copyright 1995 Elsevier.)

Table 6. Intermolecular Distances (Å)[a] and Interaction Energies (kcal/mol)[a] of the Ammonium and Tetramethyl Ammonium Cation Complexes of Benzene and Water

	C_6H_6-Me_4N^+	H_2O-Me_4N^+	C_6H_6-H_4N^+	$H_2O-H_4N^+$
R_{N-R}	4.217	3.936	2.915	2.993
$-\Delta E_0{}^B$	8.13	8.08	15.94	17.96
$-\Delta E_0$	9.66	8.98	16.99	18.93
$-\Delta E_{+,\mu}$	0.00	9.78	0.00	16.91
$-\Delta E_{+,Q}$	7.71	0.37	23.35	0.85
$-\Delta E_{+,\alpha}$	3.23	0.53	6.88	1.58
$-\Delta E_{\alpha,\mu}$	0.00	0.25	0.00	0.20
$-\Delta E_{cor}$	8.40	2.89	6.19	2.56

[a] R_{N-R} represents the nitrogen−(benzene−quadrupole/water−dipole) centroid distance. ΔE_0^B and ΔE_0 are the 100% and 50% BSSE- and ZPVE-corrected interaction energies, respectively. The individual contributions ($\Delta E_{+,\mu}$, $\Delta E_{+,Q}$, $\Delta E_{+,\alpha}$, $\Delta E_{\alpha,\mu}$) are obtained from the charge (+) of Me_4N^+/H_4N^+ and the dipole (μ), quadrupole (Q), and polarizability (α) of benzene/water. In the case of $\Delta E_{\acute{a},\mu}$, α is the polarizability of Me_4N^+/H_4N^+. The correlation energy (ΔE_{cor}) is the value of the E_e (MP2) subtracted by E_e (HF) at the MP2 optimized geometry. Taken from ref 297.

teraction and hence the resulting induction energy is magnified at the MP2 level. Minoux et al. arrived at a similar conclusion in a recent theoretical study of the interaction of the ammonium and guanidinium cations with toluene, *p*-cresol, and methyl indole.[278] Recent calculations from Pullman et al. on the interaction of the tetramethylammonium cation with other π-systems, such as pyrrole and indole, also illustrate the importance of dispersive interactions.[271] The calculations on the interactions of tetramethylammonium cation with pyridine and imidazole, wherein the nitrogen of pyridine and imidazole points to the nitrogen of tetramethylammonium cation in the lowest energy structure, indicate that caution must be exercised before generalizing the mode of interaction.[271]

In the context of organic cations interacting with different π-systems, mention should be made of the theoretical and experimental study of Berthomineu et al. on the isomerization mechanisms of metastable protonated alkylbenzenes.[299] In this study the interaction energies of the α -complexes (arene alkyl cation complexes) have been decomposed into the individual energy components. Though these energy components have been evaluated using a semiempirical method, one can readily see the effect of the presence of an extra methyl group both on the cation and the π-system. It can be seen from Table 7 that the toluene complexes are more strongly bound than the benzene complexes while the *tert*-butyl cation complexes are less strongly bound than the corresponding isopropyl cation complexes. While the former effect is due to the increased contribution of the polarization and dispersion interactions in the toluene complexes, the latter effect is mainly due to the larger contribution from the electrostatic interactions. Thus, dispersive interactions are independent of the nature of the cation but are extremely dependent on the nature of the π-system. In contrast to what is observed in the case of the interactions of metal cations with π-systems, the electrostatic energies are independent of the nature of the π-system.

Table 7. Calculated Interaction Energies for the α-Complexes (kcal/mol) of Protonated Alkylbenzenes by the Semiempirical Method

Φ→	benzene		toluene	
cation→	isopropyl	*tert*-butyl	isopropyl	*tert*-butyl
E_{el}	−8.4	−6.5	−8.6	−6.5
E_{pol}	−5.7	−4.3	−6.9	−5.0
E_{disp}	−5.0	−5.0	−6.0	−6.0
E_{rep}	5.3	4.1	6.0	4.5
$E_{tot}{}^a$	−13.9	−11.7	−15.5	−12.9
$E_{scf}{}^a$	−8.8	−6.7	−9.6	−6.9

[a] $E_{tot} = E_{el} + E_{pol} + E_{disp} + E_{rep}$. $E_{scf} = E_{el} + E_{pol} + E_{rep}$. The electrostatic term (E_{el}) is expressed as a sum of multipole interactions. The SCF electronic density of each fragment is an accurate fit of a sum of a monopole, a dipole, and a quadrupole placed at the location of each atom and each bond. The polarization term (E_{pol}) is based on the same multipole expansion as above and also includes the experimental atom- and bond-polarizability increments. The dispersion term (E_{disp}), which includes terms up to C_{10}/r,[10] is expressed as a sum of atom−atom contributions. The exchange repulsion (E_{rep}) is obtained from Rayleigh−Schrödinger perturbation theory. The SCF calculations were carried out at the HF level using a triple-ζ basis set, on the HF/3-21G optimized geometries. Taken from ref 299. The original table was in units of kJ/mol.

Ternary complexes are good models to examine the geometric and energetic effects of the neighboring molecules on the complexation. This aspect will be described in more detail in the section on water and methanol clusters. However, it would be interesting to examine these competitive effects in the context of cation−π interactions. Specifically, one would like to examine the consequences of solvation on the cation−π interaction. Thus, it would be interesting to examine the competition between cation−π, cation−solvent, and hydrogen-bond interactions prevailing in the solvent. One would expect little changes in the cation−π interaction if the solvent possesses a low dielectric. However, in the presence of a solvent like water, significant changes would result. We, however, delve on another aspect, the influence of an anion on the cation−π interaction.

Recently, Norrby and Liljefors investigated the ternary complex between benzene, ammonium cation, and formate anion (Figure 10).[280] First of all, it is apparent that stabilization energy by benzene is insufficient to shift the equilibrium to the ion pair formed, though benzene stabilizes the ion pair formed more than the proton-transferred complex by about 1 kcal/mol. The proton transfer takes place without a barrier. The experimentally evaluated interaction enthalpy of the Bz−$NH_4{}^+$ complex is about −19.3 kcal/mol. Depending on the level of theory employed, the calculated enthalpy of the Bz−$NH_4{}^+$ is in the range from −17 to −19 kcal/mol. The extent of energy lost by removing benzene from **1a** is 6.6 kcal/mol, whereas if carboxylate is first removed, subsequent removal of benzene from ammonium ion causes an energy loss of 14.1 kcalmol. The difference is 7.5 kcal/mol, whereas the destabilizing interaction between benzene and carboxylate in **1a** is only 1.3 kcal/mol, which shows that the interactions of carboxylate and benzene with ammonium are nonadditive. It can be seen from Figure 10 that the intermolecular charge transfer plays an important role in these systems. In the ion pair formed from the ammonium cation

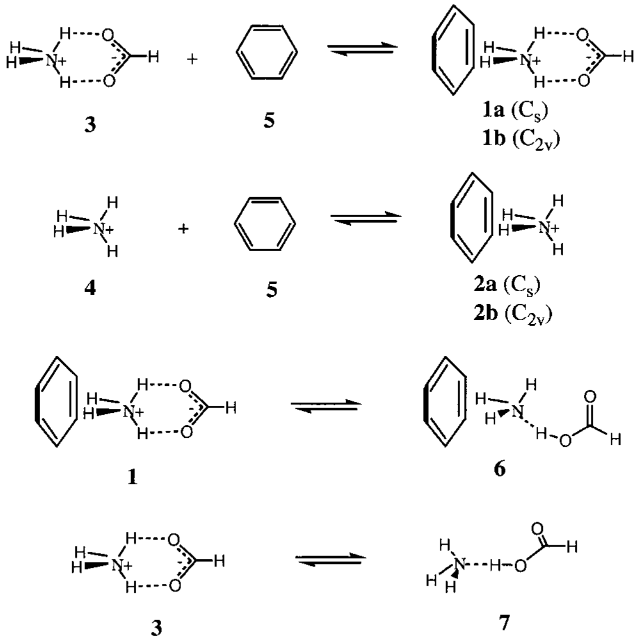


Figure 10. Calculated equilibrium structures of the ternary systems containing benzene, ammonium cation, and formate anion. In the C_{2v}-symmetric complexes (**1b** and **2b**), two ammonium hydrogens are interacting equally with bond midpoints in the benzene. The C_s complexes (**1a** and **2a**) are tilted so that only one hydrogen points toward the benzene. (Reprinted with permission from ref 280. Copyright 1999 American Chemical Society.)

and the formate anion, 0.22 e^- is transferred from the anion to the cation. Interestingly, the nitrogen and the hydrogens proximal to the formate are almost unaffected by complexation while the distal hydrogens are distinctly less positive in the complex compared to the free ammonium ion. As the distal hydrogens are involved in complexation to benzene, the charge transfer offers a reason for the lowering of the interaction energy. In the pure ammonium–benzene complex (**2b**), there is a small contribution from charge transfer to the ammonium cation by about 0.07 e^-. In the ternary complex (**1b**), the charge transfer from formate to ammonium is unchanged from **3** whereas the charge transfer from benzene to ammonium is almost absent (<0.02 e^-), indicating that the charge-accepting ability of the ammonium ion has been saturated by formate complexation.

5. *π-Complexes with Water and Methanol Clusters*

Much experimental and theoretical effort has been directed toward obtaining a quantitative description of hydrogen bonding by studying water[74,300−337] and methanol clusters.[338−357] Thus, detailed information of the hydrogen-bonding profiles of these systems have been obtained from high-resolution microwave and far-infrared spectra.[300−307,338−346] Most of the theoretical investigations of these clusters have been restricted to the determination of the most stable structures, the corresponding interaction energies, and harmonic vibrational frequencies.[308−337,347−352] Some recent reports have also tried to probe the physical origins of hydrogen bonding in some water clusters.[328,329] What is more interesting are the interactions of these methanol, water, or mixed clusters with various π-systems. In general, the structures formed by the interaction of a cation,[75,358−363] an electron, or an anion[364−368] with various water or methanol clusters bear no structural resemblance to the parent neutral water clusters due to the dominance of the strong electrostatic interactions over the much weaker H-bonding interactions present in neutral water clusters. On the other hand, in the case of the interactions of π-systems with various water[369−433] or methanol clusters,[434−444] the H-bonding interactions existing between the monomers in these clusters are much stronger than the π- or σ-type of interactions which exist between the clusters and the π-system. Thus, there are little changes in the gross structural features of the water clusters in the neutral state and in their complexed states with the π-systems. This feature is particularly exemplified in the infrared (IR) spectra and ab initio theoretical investigation of Bz–$(H_2O)_8$,[388−390] wherein it was shown that a cubic water octamer structure is π-bonded to the aromatic ring. Thus, it would be interesting to delineate the subtle changes in the H-bonding profiles of these clusters as a result of the interaction with the π-system. Another aspect which also assumes significance is on how a combination of dispersive, electrostatic, inductive, repulsive, and cooperative forces govern the interaction of the hydrogen of the water or the methanol with the π-system. Finally, we believe that these investigations would be useful in probing the role of hydrophobic interactions,[445−447] governing the conformation of proteins, the formation of micelles and biological membranes, and the immiscibility of bulk liquids.

5.1. Neutral Clusters

We briefly highlight some of the salient results of recent theoretical investigations of neutral water and methanol clusters, so that one could readily visualize the subtle changes resulting in these neutral clusters as a result of their interaction with different π-systems. Buck and Huisken review the recent experimental advances in the study of these neutral H-bonded clusters in this issue.

A large number of theoretical studies have been carried out on different sizes of water and methanol clusters.[308−333,337] The simplest water cluster, the water dimer, which has a linear structure, has been the subject of extensive theoretical studies. Kim et al. reported the intermolecular $R_{\mathrm{O-O}}$ distance to be 2.958 Å wherein anharmonic and rovibrational corrections corresponding to 0.033 Å were included based on an analytical formulation.[74] This compares very well with the experimentally determined $R_{\mathrm{O-O}}$ distance of 2.952 ± 0.004 Å.[303] The predicted dipole moment (2.61−2.63 D) is also in excellent agreement with the recently obtained experimental values of (2.60−2.64 D). The interaction energy (ΔE_e^N) was predicted to be −4.99 kcal/mol, which is in favor of the lower bound of the experimental interaction energy of −5.45 ± 0.5 kcal/mol. The anharmonic and rovibrational coupling effects are not small at 373 K. Taking into account these corrections, the predicted free energy of $\Delta G_{(T=373\mathrm{K})} = -3.39$ kcal/mol is in very

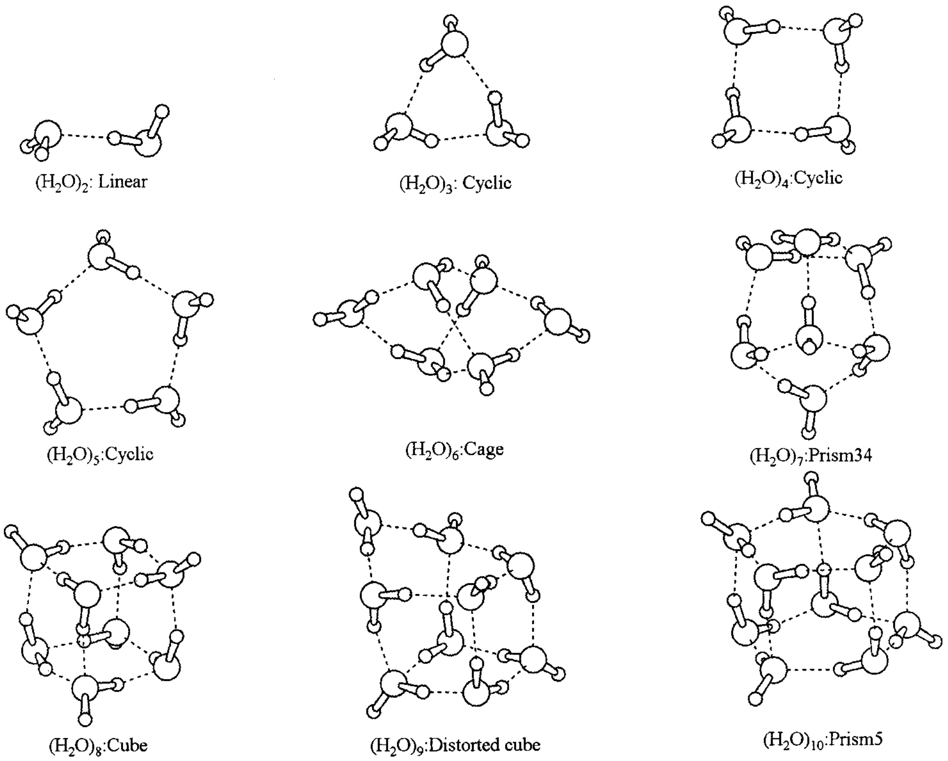


Figure 11. Glimpse of some of the minimum energy structures obtained for different sizes of water clusters.

good agreement with the experimental value of −3.34 kcal/mol.[301] The predicted interaction energies (ΔE_0^N) of $(H_2O)_2$ and $(D_2O)_2$ are −2.91 and −3.56 kcal/mol, respectively.[74]

The estimated interaction energies of these water clusters, to a large extent, depend on the size of the basis set employed and the level of correlation used. The most recent high-level theoretical study of the water dimer using massive basis sets [10s7p4d3f2g/9s4p3d2f] and [8s7p6d5f4g3h2i/7s6p5d4f3g2h] and the explicitly correlated coupled-cluster method including all single and double excitations as well as a perturbative approximation of connected triple excitations [CCSD(T)-R12] method has arrived at an interaction energy of −5.05 ± 0.07 kcal/mol.[327] These highly accurate estimates of the interaction energy clearly favor the lower bound of the experimentally determined interaction energy.[301] It is difficult to envisage similar calculations on either the larger water clusters or on their complexes with different π-systems, but it certainly leads to questions on the efficacy of methods such as the MP2, MP4, etc., in the evaluation of the various properties such as geometries, interaction energies, and vibrational frequencies of these water clusters.

The interaction energy (ΔE_e^B) of the water dimer at the MP2/aug-cc-pVDZ level is −4.46 kcal/mol.[320,321] The use of SAPT and the aug-cc-pVDZ basis set to evaluate the interaction energy ($E_{\text{int}}^{\text{SAPT}}$) of the water dimer leads to a value of −4.38 kcal/mol.[405] The lower SAPT value is due to the fact that some of the computationally tedious components of the interaction energy have not been evaluated while obtaining the final energy. It should be pointed out that SAPT results obtained using very large basis sets after inclusion of nearly all the corrections lead to a value of −4.7 ± 0.35 kcal/mol for the interaction energy ($E_{\text{int}}^{\text{SAPT}}$) of the water dimer.[50,51] Regarding the geometry, a $R_{\text{O-O}}$ distance of 2.920 Å is obtained on the MP2/aug-cc-pVDZ-optimized structure.[320] What is more important is that the level of accuracy achieved in the evaluation of the interaction energy at the MP4 level is nearly equivalent to that obtained at the MP2 level. Though the calculated dipole moments and polarizabilities of these water clusters seem to be well described at the MP2/aug-cc-pVDZ level, large deviations appear in the vibrational frequencies. Hobza and co-workers have, however, shown that these large deviations in the vibrational frequencies can be minimized by including both BSSE and anharmonic effects.[80] It, therefore, emerges from the above discussion that the choice of an adequate basis set in most cases depends on the property of interest.

As the number of water molecules increases, the global minimum energy structures of these clusters exhibit signficant changes (Figure 11). Thus, the ring structures found in the case of the trimer, tetramer, and pentamer are not the minimum energy conformers in clusters bigger than the hexamer. The hexamer in fact heralds the onset of three-dimensional minimum energy structures which suprisingly exhibit very similar energies. Thus, in the hexamer, the cage structure (global minimum) is very similar in energy to the book, prism, ring, and bag structures.[76] It can be expected that in conditions at which these clusters are formed, there is a rapid interconversion between the various isoenergetic structures. In the case of the octamer, a cage-like structure (cube) has been found to be the lowest energy conformer, a fact which has been affirmed by recent experiments.[306] It is interesting to note that using a Monte Carlo annealing technique with the MCY and CCD potentials Kim et al. obtained all the low-lying energy structures of these water clusters $(H_2O)_{4-8}$.[309]

An interesting investigation of these water clusters pertains to the contributions of various many-body terms to the total interaction energy. Thus, in the case of water clusters, the two- and three-body terms contribute to nearly 95% of the interaction energy.[309] The contribution from all the other higher order terms including relaxation effects are negligible. An elaborate review by Elrod and Saykally deals with the role of many-body effects in intermolecular interactions.[450] Gregory and Clary in a study on the contribution of many-body forces to the structure of water clusters have inferred that these forces cause a destabilization of more closed structures.[313] Hence, the minimum energy structures observed in the case of these water clusters are very much dependent on the extent of the contribution of the many-body energies. In a recent contribution, van der Avoird and co-workers decomposed the interaction energy (pair and three-body terms) into various physical contributions using SAPT.[59] Thus, the pairwise interaction energy of the global minimum is dominated by large contributions from both the attractive and exchange−repulsion terms. An important aspect of this study was that the various local minima and transition states had smaller pairwise attractions and lower pairwise repulsions with respect to the values observed in the global minimum. In particular, they noted that the decrease in the exchange−repulsion term was more important for the local minima than for the saddle points.

The methanol clusters, in contrast to the corresponding water clusters, display very different geometries. While these differences can be attributed to the presence of a single OH hydrogen in methanol, it certainly has a bearing on the geometries of the methanol clusters which bind to the π-system. Thus, most calculations indicate that ring-like structures dominate for methanol clusters as big as a decamer.[341]

A comparison of the energetics of the methanol dimer to the corresponding water dimer indicates that two methanol molecules are more tightly bound to each other than two water molecules.[74,327,350] Though the experimental intermolecular R_{O-O} distance in the methanol dimer is 2.98 Å,[344] very few theoretical studies even come close to it.[346,350−352] More significantly, the experimentally evaluated distance seems to suggest that two methanol molecules are farther apart than two water molecules in the water dimer. This is in sharp contrast to the results obtained from theoretical calculations. It would be interesting to probe the reasons for this anomaly in experimental and theoretical results. It is difficult to compare the theoretical interaction energies of the methanol and water clusters, as very few reliable studies are available at the same level of theory on both of these systems. However, calculations carried on the MP2/6-311++G**-optimized structures at the G2 level of theory by Mó et al. seem to indicate that the interaction energy (ΔE_0^N) of the methanol dimer is −3.6 kcal/mol.[350] The corresponding interaction enthalpy of −3.0 kcal/mol is in fair agreement with the experimentally determined enthalpies (−3.2 to 3.5 kcal/mol) of the methanol dimer.[342,343] On the other hand, the experimental enthalpies (−3.6 ± 0.5 kcal/mol) for the water dimer[301] indicate that the interaction energy of the water dimer is slightly greater than that of the methanol dimer. An important point which emerges from theoretical studies of the methanol clusters is the crucial contribution of electron-correlation effects to the total interaction energy. Thus, the differences in results obtained from Hartree−Fock calculations and calculations including electron correlation are more significant in the case of the methanol clusters than the water clusters. In the next section, we briefly review the available literature on the interactions of water or methanol clusters with various π-systems.

5.2. Literature Survey

The earliest theoretical study of the interaction of water with a nonpolar π-system was carried out by Del Bene in 1974.[369] Using the 4-31G basis set, the optimization of Et−H_2O and Ey−H_2O at the Hartree−Fock level yielded minimum energy geometries which are remarkably accurate for that level of calculations. However, the calculated interaction energies are expectedly low due to the noninclusion of correlation. In 1983, the first high-level calculations (which included MP2 calculations) of the interaction of ethyne with the first-row hydrides were carried out.[370] It was found that in Ey−H_2O, ethyne behaves as a proton donor. Around the same time, Karlström carried out the first ab initio calculations of the interaction of benzene with water.[17] An intermolecular potential obtained from these calculations was employed in the Monte Carlo and molecular dynamics simulations of the interaction of water with nonpolar solvents.[17,393−396] These theoretical studies were followed by the first matrix isolation studies of Ey−H_2O, Et−H_2O, and Bz−H_2O by Engdahl and Nelander. These IR investigations led to the first experimental confirmation of water being hydrogen-bonded to the π-orbital system of benzene and ethene.[371,372,375,376] In the case of the Ey−H_2O complex, it was confirmed that water behaves as a proton acceptor. Furthermore, the rotational spectral data of Klemperer and co-workers provided the first clues about the geometry of the π−H-bond in the Et−H_2O complex,[373] an aspect which was examined in more detail using microwave spectroscopy by Andrews and Kuczkowski.[374]

The two-color TOFMS study by Bernstein and co-workers was the first investigation whose aim was to probe the geometry of the Bz−H_2O complex.[179] Their results based on the 0_0^0 spectrum indicated that only a single cluster geometry was realized for this system. Interestingly, this study tried to distinguish between the H-bonding capabilities of various π-systems with molecules like NH_3 and other alkanes. A number of theoretical studies which included high-level ab initio calculations also tried to compare the geometries and interaction energies of various small molecule hydrides with benzene. The use of resonant two-photon ionization (R2PI) TOFMS by Zwier and co-workers heralded a new direction in experimental investigations of the larger Bz−H_2O clusters.[379,380] Thus, in addition to an accurate identification of the size of the water cluster bound to benzene, the rotational band analysis provided some insight into the geometry of the larger Bz−H_2O clusters. More importantly, the experimental bounds for the interaction energy ($-D_0$) of the Bz−H_2O complex were set at $1.63 < D_0 < 2.78$ kcal/mol. These studies were accompanied by model studies of the larger Bz−H_2O clusters.[396]

The fully rotationally resolved spectral study by Suzuki et al.[381] and Gutowsky and co-workers[382] provided conclusive proof of the exact geometry of the Bz−H_2O complex. The experimentally determined rotational constants were consistent with an internuclear $R_{(\mathrm{H_2O_{CM}}-\Phi_{\mathrm{CM}})}$ distance of 3.347 Å.[381] The first detailed IR spectra of the larger Bz−H_2O clusters were obtained by Zwier and co-workers for the Bz−$(H_2O)_{1-6}$ clusters.[383,384,386] The red shifts associated with the OH modes of the water clusters, apart from providing crucial insight into the Bz−$(H_2O)_{1-6}$ clusters, also helped in the elucidation of the structures of the larger water clusters.[312] The IR investigation of Silva and Devlin on the interaction of ethyne, ethene, and benzene with amorphorous ice indicated that the interaction energies are nearly twice as large as their interaction with water.[451] Cheng et al. provided an estimate of the interaction energy ($-D_0$) of the Bz−H_2O complex using the threshold difference method.[385] The value of -2.25 ± 0.28 kcal/mol obtained by them is in close agreement with the most recent and precise estimate of the interaction energy (-2.44 ± 0.09 kcal/mol) of the Bz−H_2O complex.[389] Felker and co-workers using the mass-selective, ionization-loss simulated Raman spectroscopy (IL-SRS) provided important information on the intermolecular modes of Bz−$(H_2O)_{1-5}$.[387] A notable observation made by them was that the Bz−$(H_2O)_2$ cluster exhibited particularly strong intermolecular Raman bands.[387] The most recent experimental observations pertain to the IR spectrum of the Bz−$(H_2O)_8$ and Bz−$(H_2O)_9$ clusters.[388,390,391] Thus, the Bz−$(H_2O)_8$ spectra gives a spectacular demonstration of the presence of cubic structures in water clusters, which is very different from what is observed in the case of the lower water clusters.

On the theoretical front, high-level ab initio calculations of the Bz−$(H_2O)_{n=1-3}$ clusters were carried out by Jordan and co-workers.[397] Apart from the assignment of all the OH stretch modes of the experimental spectra, they demonstrated that the water dimer exhibits the strongest interaction with the benzene ring.[397,401] Employing a combination of diffusion quantum Monte Carlo and ab initio methods, Clary and co-workers calculated the transistion states, rearrangement mechanisms, and tunneling splittings for both the Bz−$(H_2O)_1$ and Bz−$(H_2O)_2$ clusters.[398,399] Using the quantum mechanical expectation values for various configurations of the Bz−$(H_2O)_1$ complex, Kim and co-workers obtained an accurate description of the geometry and good estimates of the interaction energy.[400] Tachikawa and Igarashi tried to probe the ionization mechanisms of the Bz−$(H_2O)_1$ and Bz−$(H_2O)_2$ clusters using direct ab initio dynamics.[403] Recently, using very large basis sets and high levels of correlations, Feller arrived at an interaction energy (ΔE_0^B) of -2.9 ± 0.2 kcal/mol for the Bz−$(H_2O)_1$ complex.[77] It is interesting to highlight one of the recent theoretical studies of Felker and co-workers, wherein the various intermolecular modes of the Bz−H_2O complex were assigned by carrying out six-dimensional calculations using the filter diagonalization method.[404] A recent theoretical examination of the Bz−(H_2O) clusters by Tarakeshwar et al. tried to probe the origin of the interaction energy of the Bz−(H_2O) complex and also compared the π−H interaction in both the Bz−(H_2O) and Et−H_2O complexes.[405]

Along parallel lines, a number of investigations have been carried out on the complexes of these water clusters with other π-systems. Since the interactions of water or methanol clusters with phenol (PhOH), benzonitrile (PhCN), and purine and pyrimidine bases are mainly mediated by the ring substituents constituting them, we focus our attention on interactions involving other substituted benzenes such as fluorobenzene, *p*-difluorobenzene, and toluene and larger π-systems such as anthracene, perylene, and indole.

Extensive experimental studies employing the IR/R2PI spectroscopic method have been carried out on the clusters of various substituted benzenes by the group of Brutschy and co-workers.[407−409] A detailed description of these studies are available from the review of Brutschy in this issue. These studies indicated that the interaction of fluorobenzene and *p*-difluorobenzene with various water clusters was very different from that observed in the PhOH−$(H_2O)_n$ clusters. The effect of the fluorine substitution on the π-bonding capability of the π-system is elegantly illustrated in the theoretical calculations of Danten et al.[411] and Gallivan et al.[412] Thus, the calculations of both of these groups indicated that in the interaction of hexafluorobenzene with water, the oxygen atom of water behaves as a Lewis base and the aromatic system behaves as a Lewis acid.[411,412] On the other hand, a detailed theoretical investigation of the FBz−H_2O and DFBz−H_2O complexes by Tarakeshwar et al. indicated that unlike the Bz−H_2O system, the covalently bonded fluorine atom is involved in a σ-type of interaction with the water molecule.[413] This is very unusual because covalently bound fluorine atoms, unlike their anionic counterparts, are not known to be involved in hydrogen bonding. A very recent experimental and theoretical study of the interaction of difluoromethane with water by Caminati et al. also confirms the existence of the C−F···H−O type of interaction.[452] It would be shown later that the geometries of these fluorobenzene and difluorobenzene clusters exhibit dramatic changes when the number of water molecules are increased. The rotational spectra of the aniline−(H_2O) complex answer a very interesting question.[417] Where does the water molecule interact when confronted with both a lone pair of a heteroatom and an aromatic π-system? The structure obtained from both the rotational spectra and ab initio calculations indicates that the water hydrogens bind to the nitrogen lone pair.[417] Theoretical calculations of the pyridine–(H_2O) system yield similar results.[416] The situation becomes more interesting in the case of the interactions of these water clusters with indole. Extensive experimental studies have recently been supported by some detailed theoretical calculations on the interactions of various water clusters with various substituted indoles.[419–431] Indole, due to the presence of the pyrrole nitrogen, behaves as a H-bond donor (through the N–H group) and as an acceptor (through the π cloud). Thus, the question is where the water molecule would be bound? In the case of the indole–$(H_2O)_1$, indole behaves as a proton donor. However, in the case of the *N*-methyl indole–$(H_2O)_1$ interaction, the water molecule behaves as a proton donor.[429,430] It becomes evident that small changes in the substituents lead to spectacular changes in the nature of the interaction of these water molecules with different π-systems. The question raised in the course of the investigations of indole–(H_2O) clusters could be extended a little further. Where would the water bind if confronted with a series of coupled aromatic rings? The recent electronic spectroscopic studies of the anthracene–$(H_2O)_1$ and perylene–$(H_2O)_1$ clusters is a point in the direction of answers for this question.[416]

There have been few studies on the complexes of methanol clusters with different π-systems. Interest in the complexes of methanol clusters emerged from the realization that nucleophilic substitution reactions occur in van der Waals clusters of FBz–MeOH.[10,435,436] On the basis of the results obtained from the experimental REMPI spectra of fluorobenzene with different sizes of methanol clusters, Brutschy and co-workers concluded that nucleophilic subsitution reactions take place only when the methanol cluster size is larger than two.[434] Further studies by Maeyama and Mikami suggested that in addition to the size dependence, the orientation of the clusters is an important factor governing the progress of the reaction.[435] Recent studies by Fujii et al., which included HF/6-31G* calculations, suggested that the methanol forms a π structure with fluorobenzene. However, in recent experimental studies of methanol clusters of benzene, fluorbenzene, *p*-difluorobenzene, and *p*-chlorofluorobenzene (ClFBz), which were supported by calculations at the MP2/6-31+G* level, very interesting results were obtained on both the structures and energetics of these clusters.[443,444]

Parallel to these efforts, Zwier and co-workers extensively investigated the complexes of the methanol clusters with benzene and also the complexes of mixed water–methanol clusters with benzene. In the course of their investigations on the Bz–MeOH clusters, they also explored the intracluster ion chemistry initiated by R2PI of these complexes.[437,438] Their results showed that the Bz–$(MeOH)_3$ complex exhibits the strongest interaction of the methanol cluster to the benzene π cloud. Progressive addition of methanol molecules, however, leads to a waning of the interaction of the methanol clusters to benzene. Thus, in the Bz–$(MeOH)_5$ complex, there is no discernible interaction of the methanol cluster with the benzene π cloud. This is unlike what is observed in the case of the Bz–$(H_2O)_n$ complexes. The IR spectra of these clusters reveal some interesting features. Thus, the red shift associated with the π–H-bond in the Bz–$(MeOH)_n$ complexes are larger than those associated with the π–H bond in the Bz–$(H_2O)_n$ clusters.[439] Recently, it was shown that the frequencies associated with the methanol C–H stretching modes could also be employed to characterize the H-bonding arrangement prevailing in these clusters.[441] Investigations of ternary Bz–$(H_2O)_m$-$(MeOH)_n$ clusters seem to indicate that cooperative effects contribute to the strength of the π–H-bond formed between methanol and benzene. Moreover, the strength of the π–H-bond formed by chain-like clusters is higher than that formed by cyclic clusters of methanol and water.

5.3. Geometries

Early theoretical attempts to characterize the geometry of these complexes were generally affected by the exclusion of electron correlation in the calculations. Given this scenario, the MP2/6-31G** calculations of Bz–H_2O by Suzuki et al., which included geometry optimizations at the same level, gave a glimpse of the accuracy which could be achieved in the theoretical characterization of these π-complexes. Thus, the theoretically obtained geometrical parameters of $R_{\mathrm{CM-CM}}^{\mathrm{calcd}} = 3.195$ Å, $\Theta^{\mathrm{calc}} = 24°$ of the Bz–H_2O complex are in good agreement with the experimentally determined values of $R_{\mathrm{CM-CM}}^{\mathrm{exp}} = 3.347 \pm 0.005$ Å, $\Theta^{\mathrm{exp}} = 20°$; $\Delta\Theta = 15°$, where $\Delta\Theta$ represents the fluctuation.[381]

Kim et al., after taking into account the corrections due to anharmonicity and rovibration coupling together with a 50% BSSE corrrection, obtained a quantum mechanical expectation value of $R_{\mathrm{CM-CM}} = 3.347$ Å,$\Theta = 25°$; $\Delta\Theta = 15°$.[400] This is in excellent agreement with the experimental value. On a similar note, the predicted value of the average rotational constant $\langle B\rangle = 1990$ MHz is in good agreement with the experimentally obtained $\langle B\rangle = 1995$ MHz.[400] These results seem to indicate that an accurate intepretation of the structure of the Bz–H_2O complex can only be obtained after taking into account the wide-ranging zero-point vibrational motion.

The most recent theoretical investigation, which included optimizations at both the CCSD(T)/aug-cc-pVDZ and MP2/aug-cc-pVQZ levels, yielded $R_{\mathrm{CM-CM}}$ values of 3.235 and 3.211 Å, respectively.[77] The corresponding MP2/aug-cc-pVDZ distance is 3.240 Å.[405] It can be seen from these numbers that the use of a very large basis set or very high levels of correlation has only a marginal influence on the calculated geometries. The use of a medium-sized basis set at the MP2 level, however, yields reasonable geometries.

One of the questions which emerges from the above is on how the intermolecular $R_{\mathrm{CM-CM}}$ distance is influenced by changes in the π-system. Recent calculations from our group indicate that the MP2/aug-cc-pVDZ $R_{\mathrm{CM-CM}}$ distances for Et–, Bz–, and Tol–H_2O are 3.286, 3.227, and 3.167 Å, respectively.[405] This decrease observed in the $R_{\mathrm{CM-CM}}$ distance as one progresses from ethene to toluene can easily be

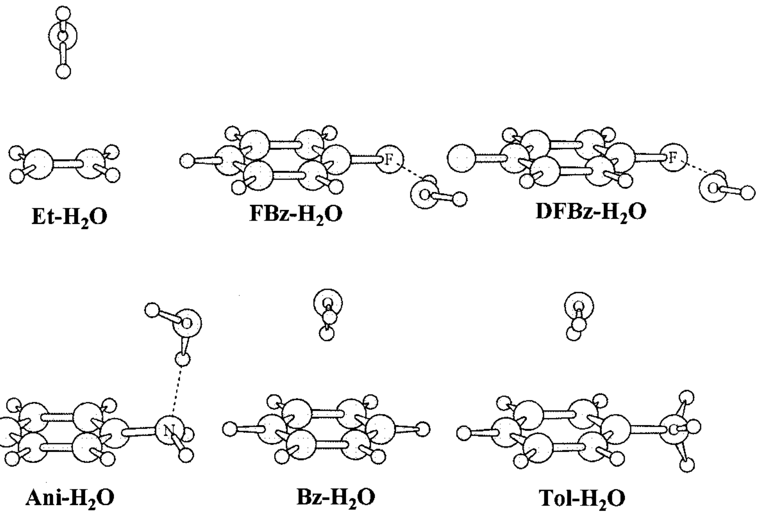


Figure 12. Minimum energy structures obtained at the MP2/aug-cc-pVDZ level for some of the complexes of the water monomer with different π-systems.

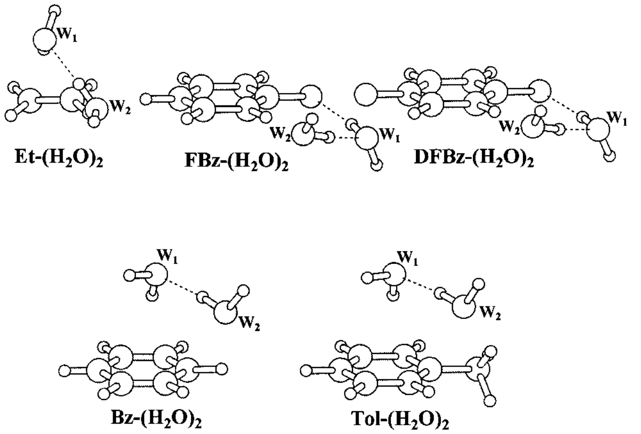


Figure 13. Minimum energy structures obtained at the MP2/aug-cc-pVDZ level for some of the complexes of the water dimer with different π-systems.

explained by the increased π densities. What happens if other subsituents are present on the phenyl ring? The presence of substituents such as fluorine or the hydroxyl or cyano groups on the phenyl ring leads to a σ-type of interaction in the case of FBz$-H_2O$, DFBz$-H_2O$, PhOH$-H_2O$, and PhCN$-H_2O$. The interactions of fluorobenzene and *p*-difluorobenzene are particularly different from either phenol or benzonitrile because their nature of interaction changes dramatically as the size of the water cluster increases (Figures 12$-$14).[413,414,448] Mention should be made of the difficulty in theoretically characterizing the exact geometry of the FBz$-H_2O$ complex.[413] This is because, both the π- and σ-type conformers of FBz are nearly isoenergetic. The characterization was, however, facilitated by the similarity of the experimental vibrational spectra of FBz$-H_2O$ and DFBz$-H_2O$. Thus, while the theoretical vibrational spectra of the σ conformers of both FBz$-H_2O$ and DFBz$-H_2O$ reproduce this trend of the experimental vibrational spectra, the spectra of π conformers are very different. The fact that the DFBz$-H_2O$ complex possesses a σ-type of conformation is affirmed by the recent experimental observations of Knight and co-workers.[449]

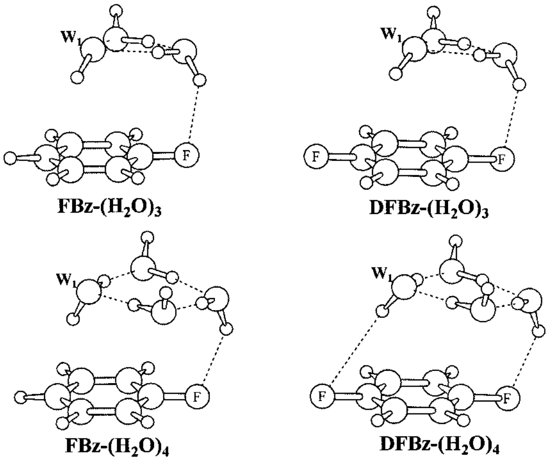


Figure 14. Minimum energy structures obtained at the MP2/aug-cc-pVDZ level for the complexes of the water trimer and tetramer with fluorobenzene and *p*-difluorobenzene.

In the case of Bz$-(H_2O)_2$, a number of high-level studies have dealt with this issue in detail. Before we discuss the results of the Bz$-(H_2O)_2$, it would be useful to have a look at how density functional theory describes the geometry of the Bz$-H_2O$ complex. Given the widespread usage of DFT methods in recent theoretical calculations of intermolecular interactions,[453$-$459] such a comparison assumes added importance.[453] The calculations of Jordan and co-workers on Bz$-(H_2O)_{1-3}$ are particularly useful in this context because comparisons have been with the MP2 method.[397] They find that the B3LYP calculations place the water monomer about 0.39 Å further from the benzene ring than the MP2 calculations. Further, the B3LYP calculations predict a much weaker interaction between benzene and water molecules. This discrepancy, though not of significance in the case of Bz$-H_2O$, becomes important in the case of interactions involving electron-deficient π-systems such as fluorobenzene or *p*-difluorobenzene.[413] Coming back to Bz$-(H_2O)_2$, the MP2 calculations of Jordan and co-workers indicate that $\pi-$hydrogen is closer to the benzene ring by about 0.06 Å than that observed in Bz$-H_2O$.[397] These findings are also supported by higher level calculations carried out by us.[405] Another observation pertains to the intermolecular O−O separation in the water dimer. Gotch and Zwier deduced from their spectroscopic results that the O−O distance of the water dimer in the Bz−$(H_2O)_2$ complex decreases by 0.20 ± 0.10 Å when compared to the neutral water dimer.[379] However, none of the theoretical calculations to date have been able to reproduce this decrease in the O−O distance.[397,399,405,414] It is interesting to note that calculations on Et−$(H_2O)_2$, Tol−$(H_2O)_2$, FBz−$(H_2O)_2$, and DFBz−$(H_2O)_2$ also indicate small decreases in the intermolecular O−O distance.[414] However, the decrease is somewhat pronounced in the case of Et−$(H_2O)_2$, FBz−$(H_2O)_2$, and DFBz−$(H_2O)_2$.

The addition of a third or additional water molecules to Bz−$(H_2O)_2$ or Tol−$(H_2O)_2$ yields some surprises regarding the minimal energy structures.[448] In the Bz−$(H_2O)_3$ complex, calculations yield two different conformers: *uud* and *udd*, which differ on whether the orientation of the free OH group is pointing up or down with respect to the OOO plane (the direction of *u* and *d* is set by benzene being placed under the $(H_2O)_3$ cycle).[401] There are small differences in the geometries and energetics of these conformers. The only important difference emerges in the frequencies associated with the free OH groups.

In the context of higher water clusters making a transition from a σ- to a π-type of interaction with the π-system, mention should be made of the interaction of indole and *N*-methyl indole with water clusters.[429−431] In a detailed and extensive investigation, Carney et al. showed that while indole (Ind) has a σ-type of interaction with a single water molecule, a π−H-bond is formed in the case of the interaction involving *N*-methyl indole. In the case of the Ind−$(H_2O)_2$ system, the indole has a π-type of interaction with the acceptor water and a σ-type of interaction with the donor water molecule. The complexes of the water trimer with *N*-methyl indole reveal some interesting features regarding their conformations. Thus, two conformers which only differ in the orientation of the H-bonds (clockwise or counterclockwise) in the water trimer cycle relative to the indole plane are possible. Though the interaction energies are very similar for both these conformations, these two conformers can be distinguished in the experiments based on their spectral characteristics. This is very interesting, especially in the context of chiral discrimination.[460]

Similar to what is observed in the case of the Ind−$(H_2O)_2$ clusters, there is a dramatic change in the minimum energy structures of the $(H_2O)_3$ complexes of fluorobenzene and *p*-difluorobenzene.[448] In sharp contrast to the σ-type of structures exhibited by the FBz−$(H_2O)_2$ and DFBz−$(H_2O)_2$ complexes, the FBz−$(H_2O)_3$ and DFBz−$(H_2O)_3$ complexes exhibit a transition to π-type of structures. Though the σ-type of interaction to the F atom is still present in these complexes, it is markedly weaker than what is observed in the complexes of the water monomer and dimer with fluorobenzene and *p*-difluorobenzene. As in the complexes of the water trimer with *N*-methyl indole, the FBz−$(H_2O)_3$ and DFBz−$(H_2O)_3$ complexes also exhibit two conformations which differ in the orientation of the H-bonds. The differences in the geometries of these two different conformers are limited to the F···H and O−O distances. However, the interaction energies of these two conformers reveal that they are isoenergetic. It should also be mentioned that the semiempirical calculations of Brenner and co-workers on the complexes of water clusters with *p*-difluorobenzene are surprisingly very accurate regarding the minimal energy geometries of these complexes.[410] Though a number of calculations have been carried out on the complexes of the larger water clusters with benzene, all of them yield no surprises regarding the geometries.

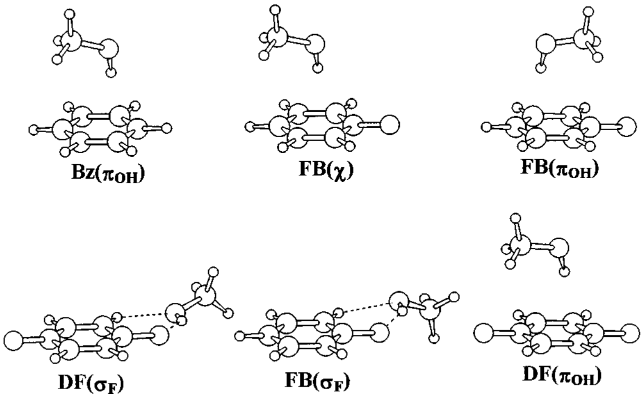


Figure 15. Minimum energy structures obtained at the MP2/6-31+G* level for the complexes of the methanol monomer with benzene, fluorobenzene, and *p*-difluorobenzene.

Only a few theoretical studies have dealt with the geometries and interaction energies of the complexes of these π-systems with methanol clusters. The emphasis of most of the theoretical studies on the Bz−$(MeOH)_n$ clusters until now has been the assignment of the experimental vibrational frequencies. However, the first theoretical investigation carried out using empircal potentials by Garrett et al. reveals some interesting features of these complexes.[437] While the gross structural characteristics of Bz−$(H_2O)_{1,2}$ and Bz−$(MeOH)_{1,2}$ are very similar, they are different for the larger clusters. These changes can easily be attributed to the absence of a second hydrogen in methanol. As a result, while the cyclic water trimer can still form a π−hydrogen bond through one of its free hydrogens, the cyclic methanol trimer cannot do so. As a result, in the Bz−$(MeOH)_3$ complex the methanol trimer possesses a linear structure. Recently in an experimental and theoretical study of the interactions of fluorobenzene and *p*-difluorobenzene, Buchhold et al. evaluated the geometries and interaction energies of the methanol monomer complexes of benzene, flurobenzene, and *p*-difluorobenzene at the MP2/6-31+G* level (Figure 15).[443] The calculated geometries indicate that the methanol oxygen in the Bz−MeOH complex ($R_{\Phi CM-O}$ = 3.318 Å) is much closer to the benzene center of mass than the water oxygen in the Bz−(H_2O) complex ($R_{\Phi CM-O}$ = =3.380 Å). This contrasts with what is observed in the case of the water and methanol

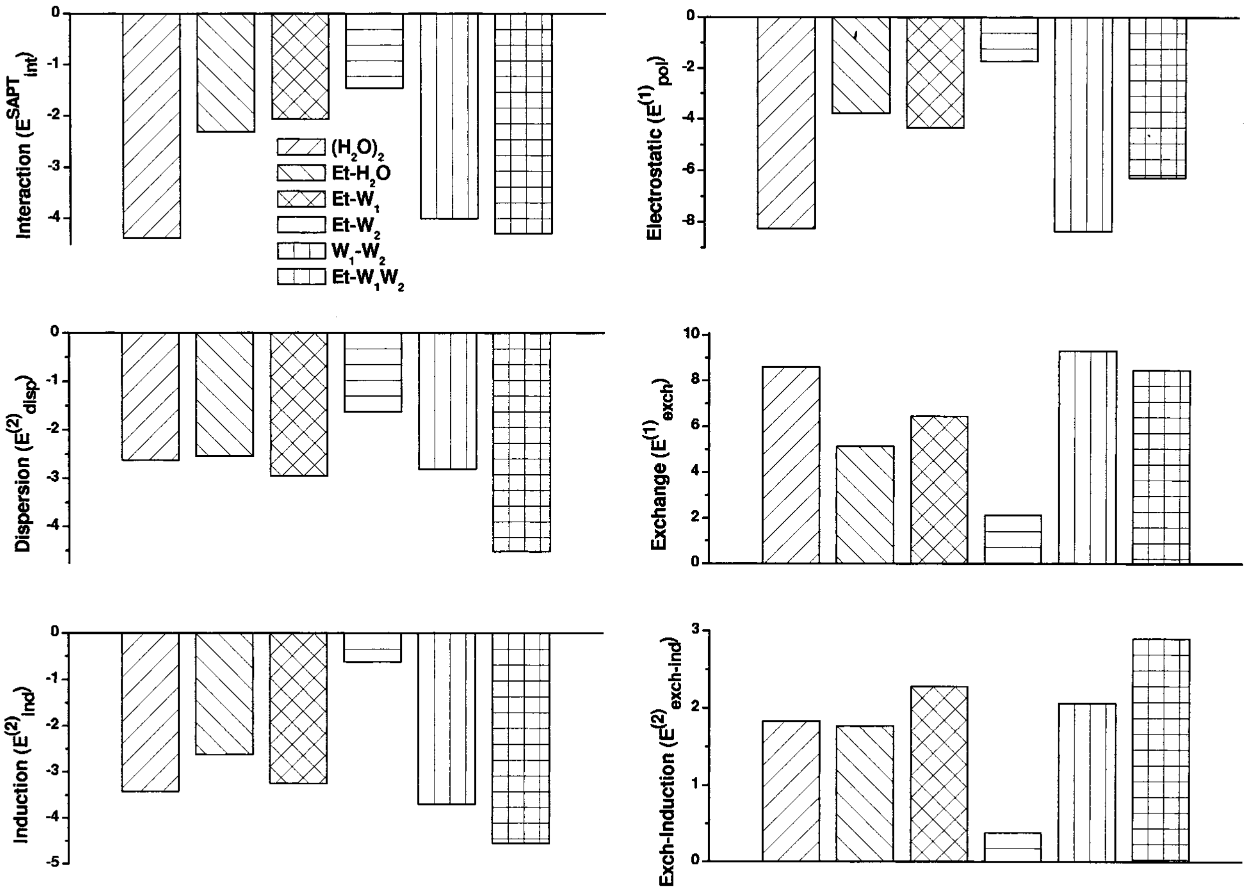


Figure 16. Comparison of different components of the interaction energy of the water dimer and the complexes of ethene with the water monomer and dimer obtained using the aug-cc-pVDZ basis set.

dimers, with the intermolecular distance being comparatively smaller in the case of the water dimer.

5.4. Energies

Since the experimental determination of the interaction energy of the Bz−H_2O complex by Gotch and Zwier[379] and later by Cheng et al.[385] and Courty et al.,[388] a number of theoretical investigations have evaluated the interaction energy at different levels.[77,397,398,400,405] Kim et al. obtained a value of −2.74 ± 0.68 kcal/mol for the interaction energy (ΔE_0) of the Bz−H_2O complex.[400] The best estimate of the interaction energy (ΔE^B_e) of the Bz−H_2O complex is −3.9 ± 0.2 kcal/mol.[77] After ZPVE corrections, the interaction energy (ΔE^B_0) is found to be −2.9 ± 0.2 kcal/mol, which is in reasonable agreement with the most recent experimentally determined energy of −2.44 ± 0.09 kcal/mol.[389] How do changes in the π-system influence the energies of the resulting H_2O complex? A comparison of the ZPVE- and BSSE-corrected interaction energies at the MP2/aug-cc-pVDZ level for a number of π-complexes seem to indicate that it is more tightly bound to toluene than to either benzene or ethene.[448] Though the high interaction energy of the Tol−H_2O can easily be attributed to the increased electron density of the π-system, the surprisingly high interaction energy of the Et−H_2O complex is harder to explain. The ethene π-system is composed of only two π electrons, while the benzene π-system is composed of six π electrons. If one attributes the π−H bonding interaction as resulting purely from electrostatic forces prevailing between the water hydrogen atom and the π electrons, the Et−H_2O interaction energy (ΔE_0) should be less strong than that calculated at −1.60 kcal/mol. This leads to the question, which we believe is vital in understanding the π−H interaction, of whether the stronger interaction in Et−H_2O complex results from an extra stabilization or the relatively weaker interaction in Bz−H_2O emerges from a destabilizing interaction. The answer to this question and the origin of the stabilizing and destabilizing interactions can be obtained from a comparison of the individual energy components of the interaction energy.

In this context it is interesting to examine how the energetics of π−H-bonding differs from conventional hydrogen bonding. The results obtained from a SAPT analysis of the components of the interaction energy of both the water dimer and the Et−H_2O complex are plotted in a histogram (Figure 16). Using the aug-cc-pVDZ basis set, one notices that the SAPT interaction energy (E^{SAPT}_{int}) of the water dimer is −4.38 kcal/mol.[405] A significant attractive contribution to the interaction energy of the water dimer results from electrostatic contributions (E^1_{pol} = −8.25 kcal/mol). The contributions from the dispersion and induction terms are comparatively smaller. On the other hand, the electrostatic contribution to the interaction energy of the Et−H_2O complex (E^1_{pol} = −3.78 kcal/mol) is only about 40% of the E^1_{pol} found in the water dimer. While the contributions from the dispersion energies are nearly similar in the case of both the water dimer and the Et$-$H$_2$O complex, it is more significant in the latter. As a result, one observes that nearly 83% of the total interaction energy of the water dimer is accounted at the Hartree$-$Fock level, but in the case of the Et$-$H$_2$O complex, only 31% of the total interaction energy is accounted at the Hartree$-$Fock level. What, however, distinguishes between the two types of interactions are the exchange repulsion energies ($E^1_{\mathrm{exch}} = 8.60$ kcal/mol for the water dimer and $E^1_{\mathrm{exch}} = 5.12$ kcal/mol for the Et$-$H$_2$O complex) which are very different. Though this difference could be attributed to the increased intermolecular separation in Et$-$H$_2$O ($R_{\mathrm{H}-||_{CM}} = 2.376$ Å) than in the water dimer ($R_{\mathrm{H_d-O_a}} = 1.946$ Å; where $||$, H$_d$, and O$_a$ represent the C$-$C double bond, donor hydrogen, and acceptor oxygen, respectively), subtle differences in the values of the repulsive terms seem to govern the energetics and hence the geometrical preferences of complexes exhibiting the $\pi-$H type of interaction.

This argument is illustrated in more detail in the case of the Et$-$(H$_2$O)$_2$ complex.[414] We initially compare the Et$-$W$_1$, Et$-$W$_2$, and Et$-$H$_2$O interactions, followed by a comparison of Et$-$W$_1$W$_2$ and Et$-$H$_2$O. Here, W$_1$ and W$_2$ denote the acceptor and donor water molecules of the water dimer interacting with Et in the Et$-$(H$_2$O)$_2$ complex. It can be seen from Figure 16 that there is a decrease in the SAPT interaction energy ($E^{\mathrm{SAPT}}_{\mathrm{int}}$) from -2.31 to -2.07 kcal/mol when one progresses from Et$-$H$_2$O to the Et$-$W$_1$ complex. This energetic decrease is associated with a decrease in the intermolecular separation ($R_{\mathrm{H}-||_{CM}} = 2.365$ Å) observed in the Et$-$W$_1$ complex. A look at the energy components reveals that the small increase in the attractive energy components ($E^1_{\mathrm{pol}} = -4.33$ kcal/mol; $E^2_{\mathrm{ind}} = -3.24$ kcal/mol; $E^2_{\mathrm{ind}} = -2.95$ kcal/mol) is overwhelmed by the large increase in the exchange repulsion term ($E^1_{\mathrm{exch}} = 6.45$ kcal/mol). More interesting are the energies observed in the case of the Et$-$W$_2$ complex. Though there is a large decrease in the attractive energy components, this decrease is also compensated by a large decrease in the repulsive energies ($E^1_{\mathrm{exch}} = 2.11$ kcal/mol; $E^1_{\mathrm{exch-ind}} = 0.38$ kcal/mol). In the case of Et$-$W$_1$W$_2$ (the dimer is considered as a single molecule), one notices that the individual interaction energy terms can nearly be approximated as the sum of the interaction energy terms of the Et$-$W$_1$ and Et$-$W$_2$ interactions (~80%) and a small correction term (~20%) to account for the W$_1$W$_2$ interaction. On the basis of the above discussion, it can be inferred that the structure and hence the interaction energy of the Et$-$(H$_2$O)$_2$ complex is controlled more by the contributions from the repulsive than the attractive terms. This is particularly important regarding the position of W$_2$ with respect to W$_1$ and Et.

Since SAPT calculations using the aug-cc-pVDZ basis set could not be carried out on the Bz$-$H$_2$O complex, we briefly compare the results obtained for both the Et$-$H$_2$O and Bz$-$H$_2$O complexes using the 6-31+G* basis set in the histogram (Figure 17). It should be noted that the use of small basis sets and low levels of theory only affects the accurate evaluation of the dispersion terms. Even in the case of the evaluation of the dispersion terms, the relative trends would not be altered by the use of higher levels of theory and large basis sets. Figure 17 reveals that the major difference in the interaction energy of Et$-$H$_2$O and Bz$-$H$_2$O complexes arises from the dispersion terms.

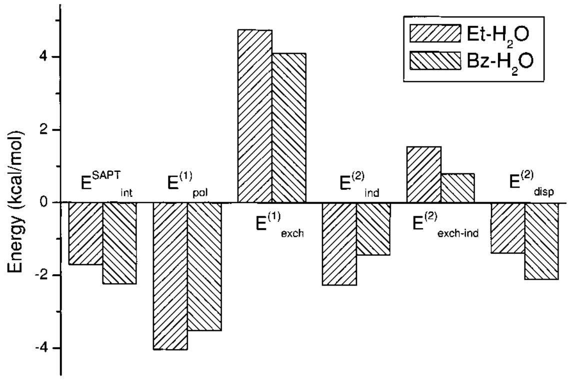


Figure 17. Comparison of different components of the interaction energy of the complexes of the water monomer with ethene and benzene obtained using the 6-31+G* basis set.

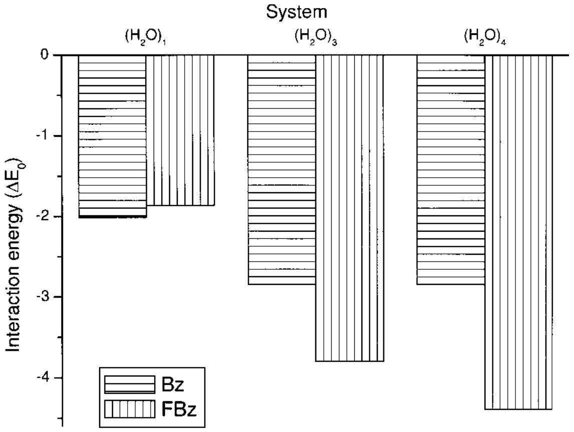


Figure 18. Comparison of the interaction energies of the complexes of benzene and fluorobenzene with different sizes of water clusters.

Calculations on the Bz$-$H$_2$O complexes seem to indicate that the $\pi-$H interaction energy decreases as additional water molecules are added to the water cluster binding to the π-system.[397,401,448] A question which arises from the above observation is whether this is a general rule or not. A discussion of the results obtained on the FBz$-$(H$_2$O)$_{3,4}$ and DFBz$-$(H$_2$O)$_{3,4}$ systems is useful in this regard. It can be seen from Figures 12$-$14 that in sharp contrast to what is observed in FBz$-$(H$_2$O)$_{1,2}$ and DFBz$-$(H$_2$O)$_{1,2}$, the higher clusters exhibit a $\pi-$H type of interaction. Essentially this seems to indicate that $\pi-$H-bonding becomes more favorable as the size of the water cluster binding to either fluorobenzene or p-difluorobenzene increases. Though it is difficult to decompose the interaction energy of these systems, we have tried to illustrate the differing trends of the Bz$-$(H$_2$O)$_{1-4}$ and FBz$-$(H$_2$O)$_{1-4}$ clusters in Figure 18. It can be easily noticed that the interaction of the water tetramer with the π-system is stronger in

Table 8. Comparison of the Binding Energies and Selected Geometrical Parameters of π- and σ-Conformers of the Substituted Benzene−Water/Methanol Complexes at the MP2/6-31+G* Level (Taken from refs 405 and 413)[a]

	Bzπ_{OH}		**FBπ_{OH}**		**FBσ_F**		**DFπ_{OH}**		**DFσ_F**	
	H_2O	MeOH	H_2O	MeOH	H_2O	MeOH	H_2O	MeOH	H_2O	MeOH
$-\Delta E_e^B$	2.22	2.56	1.75	2.25	3.13	3.15	0.89	1.37	3.23	3.30
$-\Delta E_0^B$	0.89	1.39	0.70	1.46	1.80	2.28	0.37^b	1.02^c	1.91	2.46
$-\Delta E_e$	3.34	4.00	2.91	3.75	4.01	4.09	2.02	2.81	4.12	4.24
$-\Delta E_0$	2.01	2.83	1.86	2.96	2.68	3.22	1.50^b	2.46^c	2.80	3.40
$-\Delta E_{cor}$	2.97	4.94	2.89	5.05	2.12	2.54	2.57	4.67	2.10	2.52
$-\Delta E_{es}$	7.11	5.66	4.81	4.42	8.16	7.29	1.27	1.19	8.50	7.86
$R_{O\cdots\Phi_{CM}}$	3.380	3.318	3.473	3.433	4.142	4.166	3.490	3.387	4.496	4.506
$R_{H\cdots\Phi_{CM}}$	2.508	2.370	2.690	2.578	3.678	3.660	2.583	2.452	4.167	4.139
$R_{H\cdots F}$					2.093	2.086			2.137	2.128
$R_{O\cdots\Phi_H}$					2.367	2.393			2.318	2.326
$\boldsymbol{r}_{OH}$	0.974	0.974	0.974	0.974	0.974	0.974	0.973	0.973	0.974	0.974

[a] All energies are in kcal/mol; distances are in Å; frequencies are in cm^{-1}. See Figure 15 for conformer definitions. ΔE_e^B and ΔE_e are the 100% and 50% BSSE-corrected interaction energies, respectively. ΔE_0^B and ΔE_0 are the ZPVE-corrected ΔE_e^B and ΔE_e. The frequencies for ZPVE correction were evaluated at the MP2/6-31+G* level. The electron correlation energy ΔE_{cor} is the value of the E_e (MP2) subtracted by E_e (HF) at the MP2 optimized geometry. ΔE_{es} is the electrostatic (charge−charge) interaction energy evaluated using NBO charges evaluated on the MP2 densities. $R_{O\cdots\Phi_{CM}}$ and $R_{H\cdots\Phi_{CM}}$ are the substituted benzene center-of-mass to water/methanol oxygen and hydrogen (involved in the formation of H-bond or π H-bond) distances, respectively. $R_{H\cdots F}$ is the fluorine to water/methanol hydrogen distance and $R_{O\cdots\Phi_H}$ is the water/methanol oxygen to the nearest substituted benzene hydrogen distance in the σ_F conformers. $\boldsymbol{r}_{OH}$ is the water/methanol OH bond distance. [b] Single imaginary frequency of 75.9 cm^{-1} ignored while evaluating ZPVE. [c] Single imaginary frequency of 61.7 cm^{-1} ignored while evaluating ZPVE.

FBz−$(H_2O)_4$ than in Bz−$(H_2O)_4$. While it may be argued that the additional stabilizing interactions in the form of a σ−H-bond with the covalently bonded fluorine might be responsible for this increase, it should also be noted that the formation of a σ−H-bond involving the aromatic fluorine atom decreases its electron-withdrawing capabilitiy. As a result, the π−H interaction which was energetically disfavored in the complexes of fluorobenzene and *p*-difluorobenzene with the lower water clusters becomes more favorable when the size of the water cluster increases.

Though the minimum energy structure of the Bz−H_2O complex (C_s symmetry) possesses only a single π−H bond, vibrational averaging due to an almost free rotation of the water about the benzene 6-fold axis renders the hydrogens indistinguishable. In their paper, Augspurger et al. suggested that the potential-energy surface is flat with respect to the exchange of the protons in the hydrogen bond, and hence, tunelling is probable between the two isoenergetic C_s minima.[396] The tunneling dynamics and the associated splittings of the Bz−H_2O and Bz−$(H_2O)_2$ complexes have been calculated from quantum simulations with the diffusion Monte Carlo (DMC) approach by Clary and co-workers.[398,399] On the basis of the DMC results and ab initio calculations, three distinct rearrangements were found to be feasible for the tunneling splittings. These include the C_6 tunneling, hydrogen exchange, and ring reversal in the case of the Bz−H_2O complex and the internal rotation, hydrogen flip, and hydrogen flaps in the case of the Bz−$(H_2O)_2$ complex.[399] They found that the predicted splitting patterns are extremely dependent on whether empirical potentials or ab initio calculations have employed in their evaluation. The predicted tunneling splittings have, however, not been observed experimentally for the Bz−H_2O complex. A single tunneling splitting was, however, experimentally identified in the case of the Bz−$(H_2O)_2$.

Coming to the methanol clusters, the MP2/6-31+G* interaction energy (ΔE_0) of the Bz−MeOH complex is −2.83 kcal/mol, which is higher than the corresponding interaction energy (ΔE_0) of −2.01 kcal/mol observed in the case of the Bz−H_2O complex (Table 8).[443] The increase in the interaction energy of the Bz−MeOH complex is in contrast to the electrostatic energies. Thus, the electrostatic energy (ΔE_{es}) in the case of the Bz−H_2O complex (−7.11 kcal/mol) is higher than that observed in the Bz−MeOH complex (−5.66 kcal/mol). The correlation contribution (ΔE_{cor}) of −4.94 kcal/mol, however, compensates for the decreased electrostatic contribution in the Bz−MeOH complex. A similar increase in the interaction energy of the methanol clusters over that of the water clusters is also observed in the case of the σ-complexes of fluorobenzene and *p*-difluorobenzene.[443]

The interaction energies exhibited by the ClFBz−MeOH complexes give particular insight into the energetics of systems where multiple H-bonding sites are present.[444] Thus, as mentioned earlier, the three conformers (Figure 19) of the ClFBz−MeOH complex (all of which are stable minima, characterized by positive vibrational frequencies) exhibit different energies. Thus, the interaction energies (ΔE_0) at the MP2/6-31+G* level seem to indicate that the σ_{Cl} and π conformers are isoenergetic (−2.45 kcal/mol) but the σ_F conformer (−3.38 kcal/mol) is lower in energy than the other two conformers. This discrepancy in energetics, however, can be resolved by the use of larger basis sets. What is interesting, however, is the fact that while the corresponding π conformer of DFBz−MeOH,[443] whose interaction energy (ΔE_0) is −2.46 kcal/mol (the ZPVE calculation neglects the contribution of the imaginary frequencies), is not a stable minimum (characterized by an imaginary frequency), the ClFBz−MeOH complex is a stable minimum. Experimental evidence indicates the presence of the π conformer in the ClFBz−MeOH complex and the absence of the same in the DFBz−MeOH

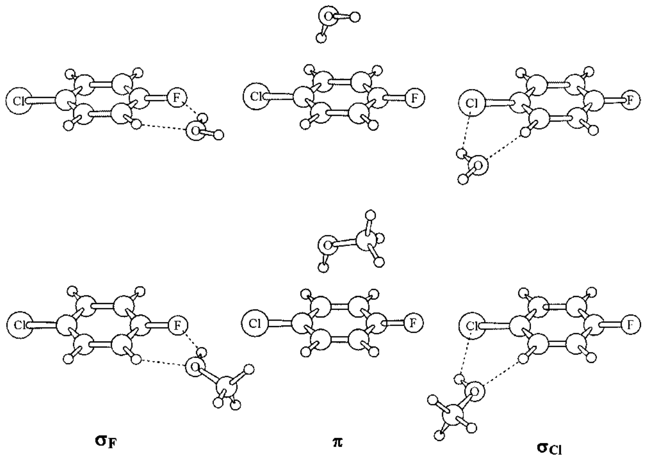


Figure 19. Different conformers obtained at the MP2/6-31+G* level for the complexes of the *p*-chlorofluorobenzene with the water and methanol monomers.

complex. The effect of the nature of the substituent on the energetics and the geometries exhibited by the minimum energy conformers is exemplified in the above example.

To distinguish the characteristics of the methanol and water complexes of *p*-chlorofluorobenzene, we recently carried out a theoretical investigation of the ClFBz−H_2O complexes.[448] It can be seen from Figure 20 that though the differences in the electrostatic contributions to the interaction energy are very small, the correlation contributions are very high in the case of the methanol complexes. Particularly one can notice the marked increase of the correlation contribution in the case of the π conformer of the ClFBz−MeOH.

5.5. Vibrational Frequencies

The experimental vibrational frequencies are sensitive probes of the cluster structure,[11,383,388] and hence, theoretical evaluations of the same enable one to confirm the identity of the structure.[461] Additionally, these frequencies also help understand the effects of subtle modifications of the cluster structure. These modifications could include the presence of additional water or methanol molecules or substituents on the π-system. In contrast to the complexes of these π-systems with cations, rare gases, and dihalogens, the determination of the structures of the complexes of these water and methanol clusters has been extensively aided by both the calculation and experimental determination of the vibrational spectra. Moreover, the availability of detailed spectral information of the corresponding neutral clusters facilitates an understanding of the effect of the presence of the π-system on the spectra.

Thanks to the contributions of Zwier and coworkers, a large body of spectral information is available on the complexes of Bz with both water and methanol clusters.[383,384,386,388,390,391.397,401] This information has been very valuable in the study of the fundamental H-bonding topologies of these water and methanol clusters. More important has been the insight into the perturbing effects of Bz on these water and methanol clusters. As said earlier, a comparison of the experimental frequencies, which includes anharmonic contributions to the calculated harmonic frequencies, is tenuous. More useful is a comparison of the experimental and theoretical frequency shifts. The groups of Jordan and Zwier did that and obtained an elaborate picture of the changes resulting in the OH frequencies of these water clusters as a result of their complexation with Bz.[397,401] Interestingly, the harmonic vibrational frequencies evaluated using the B3LYP functional seem to indicate that the trends in the OH spectra of water and Bz−$(H_2O)_n$ clusters are faithfully reproduced. However, the magnitude of shifts of single-donor OH stretch frequencies are exaggerated.

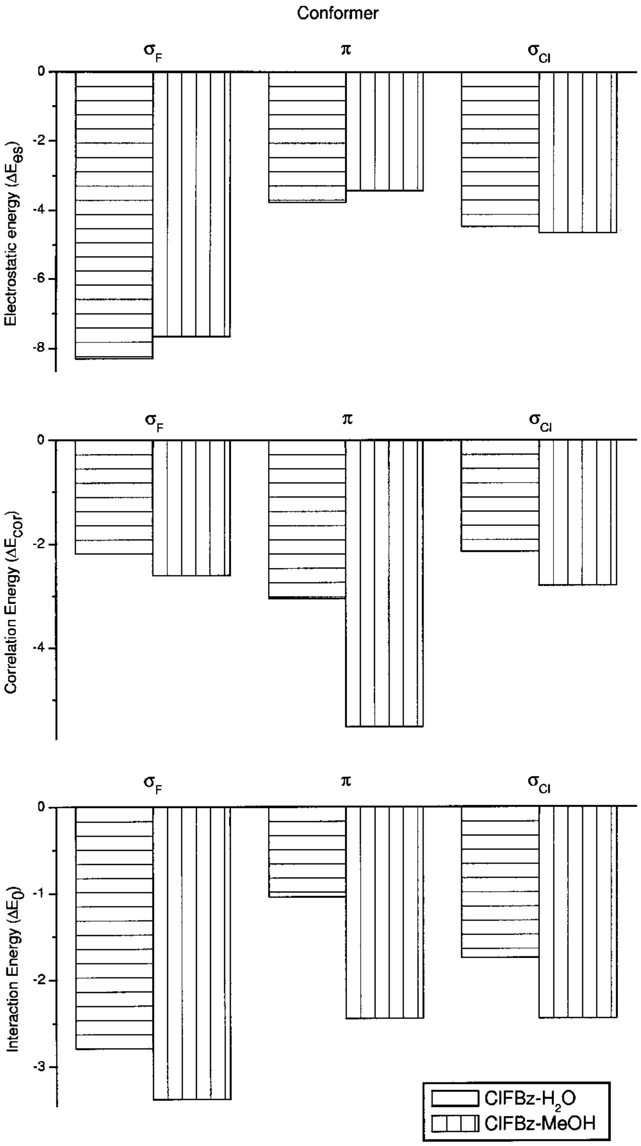


Figure 20. Comparison of the interaction, electrostatic, and correlation energies of different conformers of the *p*-chlorofluorobenzene−water and *p*-chlorofluorobenzene−methanol complexes obtained at the MP2/6-31+G* level.

The OH frequencies of water in the Bz−H_2O complex exhibit a red shift when compared to water in its monomeric state. The MP2-predicted red shift of 20 cm^{-1} for the OH stretching frequencies of the Bz−H_2O complex is in excellent agreement with the experimentally observed red shifts of 25 and 23 cm^{-1}.[397] One of the interesting features of the OH stretching frequencies are the changes in their intensities. Thus, in the $Bz-H_2O$ complex, the experimental asymmetric to symmetric stretch intensity ratio of the OH frequencies is about 1.5, which is far less than the corresponding ratio of 14.5 observed in the water monomer. While this enhancement of the intensity of the symmetric stretch is reproduced in the theoretical calculations, much interest has been evinced on the origin of this enhancement. Two explanations have been offered to explain the same.[397] Thus, it was suggested the intensity change could be due to either a partial localization of the OH stretch vibrations in the complexed state or induction. Calculations, however, reveal that the former explanation is not right. Support for the latter explanation comes from the enhancement of the dipole moment of the water in the complexed state.

In the $Bz-(H_2O)_2$ complex, there are some interesting changes in the OH spectra of the water dimer. Apart from a red shift in one of the symmetric stretches of the water dimer due to formation of a $\pi-$hydrogen bond, a large red shift is associated with the donor H-bonded OH group. This red shift is easily explained by the increase of the donor O−H bond length as a result of the decreased O−O separation. In the next section on the charges we show that this decrease is associated with an increase in the electron charge density between the oxygen atoms of the water dimer. The calculated spectra of the *uud* and *udd* conformers of the $Bz-(H_2O)_3$ complexes indicates that there are very small changes in the frequencies associated with the OH modes.[401] Given the calculated energy difference of 0.6 kcal/mol between the two conformers and hence the rapid interconversion, it is unlikely that two distinct conformers can be observed in the experimental spectra. Indeed, the experimental spectra indicate the presence of only a single conformer. One, however, notices that despite the significant differences in the $R_{\Phi_{\text{CM-H}}}$ distances of the two conformers, the frequencies associated with the $\pi-$H mode are the same. In the case of the $Bz-(H_2O)_6$ complex, Lee et al. recently observed that there are little changes in the IR spectral features of both $(H_2O)_6$ and $Bz-(H_2O)_6$ complexes.[433] Their theoretical study indicates that in the $Bz-(H_2O)_6$ complex, the water hexamer possesses a cage structure. Furthermore, they were able to identify the particular cage conformer responsible for the experimental spectra of the $Bz-(H_2O)_6$ complex based on an analysis of the calculated IR spectra of several isoenergetic cage conformers.[433] Progressing to the $Bz-(H_2O)_8$ complex,[388,390] the calculated spectra of the S_4 and D_{2d} conformers seem to be in agreement with the experimental observation of two different isomers. Interestingly, apart from the characteristic red shift associated with the $\pi-$H bond, very little differences are observed in the spectra of corresponding neutral water clusters and the $Bz-(H_2O)_8$ complexes. A similar situation prevails in the $Bz-(H_2O)_9$ complexes wherein the three different isomers observed in the experiment can be associated with three different conformers.[391] An important point which emerges from the above calculations of the OH spectra is that as one progresses from $Bz-(H_2O)_1$ to $Bz-(H_2O)_9$, the single-donor OH modes are more affected by the presence of benzene than the double-donor OH modes.

Against the background of these results on the OH spectra of the $Bz-(H_2O)_n$ complexes, it is useful to examine the features of the OH modes in the H_2O complexes of other π-systems. In the case of the $Et-H_2O$ complex, the red shift associated with the π-bonded OH mode is smaller than that observed in the $Bz-H_2O$ complex.[372,375] On the other hand, one observes a larger red shift in the case of the $Tol-H_2O$ complex.[409] The above observations seem to indicate that red shifts associated with the π H-bond can be correlated with the electron density of the π cloud. On the basis of a number of calculations of hydrogen-bonded complexes of HF, Liu and Dykstra concluded that the changes in the vibrational frequencies of HF are primarily a consequence of (i) the mutual, linearly varying part of the electrical interactions of the species in the complex and (ii) the intrinsic anharmonicity of the HF potential curve.[462] Since the electrical interaction can easily be determined from the monomer electrical properties, the vibrational frequency shifts could be correlated directly to the monomer properties.[462] We find that their conclusions are valid because we recently observed that the red shift associated with the formation of a $\pi-$H-bond can be correlated to the electrostatic energy E^1_{pol}.[414]

In the case of the $FBz-H_2O$ and $DFBz-H_2O$ complexes, the experimental red shifts are nearly identical but smaller than that observed in the case of the $Bz-H_2O$ complex.[409] This red shift was initially attributed to the formation of a $\pi-$H-bond. However, detailed calculations indicate that the formation of a H-bond to the covalently bound fluorine atom leads to this red shift.[413] Incidentally, the $\pi-$H-bonded conformer of the $FBz-H_2O$ complex is isoenergetic to the corresponding σ conformer. Hence, it was only a knowledge of the vibrational frequencies which lead to the correct assignment. A question which can be raised after this discussion of the OH shifts is on the efficacy of these theoretical methods in describing different types of H-bonds in different π-systems. In Figure 21 we plot the experimentally obtained and theoretically predicted frequencies of the OH stretching modes of the $Et-(H_2O)_2$, $Tol-(H_2O)_2$, $Bz-(H_2O)_2$, $FBz-(H_2O)_2$, and $DFBz-(H_2O)_2$ systems. It can be seen that while shifts associated with the donor OH modes are well-reproduced, discrepancies arise in those associated with the $\pi-$H-bond. Interestingly, calculations done using a larger basis set seem to obliterate this discrepancy to a small extent.

Given the results on the OH stretching modes of the water clusters, it is of interest to examine how the methanol OH modes are affected by their interaction with various π-systems. The red shift associated with the π-bonded methanol OH mode is greater than what is observed in the case of the π-bonded water mode. This increase has been ascribed to the stronger $\pi-$H-bond which can be correlated to the increased polarizability of methanol. In the case of the interaction of methanol with fluorobenzene and

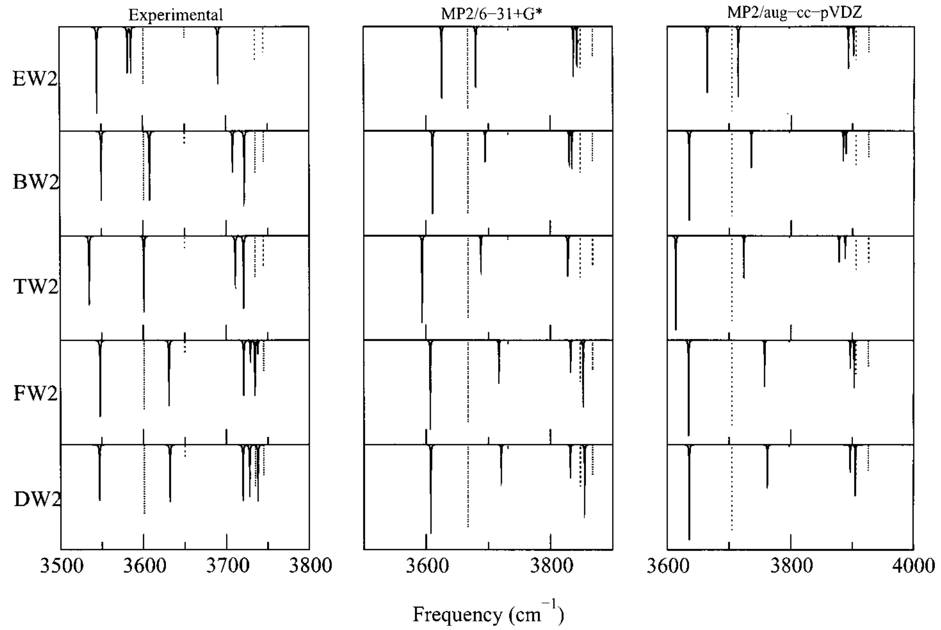


Figure 21. Calculated and experimental (IR) frequencies of the OH stretching modes of the water dimer (W2) in its complexes with ethene (EW2), benzene (BW2), fluorobenzene (FW2), *p*-difluorobenzene (DW2), and toluene (TW2).

Table 9. MP2/aug-cc-pVDZ NBO Charge Shifts (au) of the Oxygen and Hydrogen Atoms of the Water Monomer in the Complexes Formed with Ethene (Et), Benzene (Bz), Toluene (Tol), Fluorobenzene (FBz), *p*-Difluorobenzene (DFBz)[a]

atom	Et−H_2O	Bz−H_2O	Tol−H_2O	Fbz−H_2O	DFBz−H_2O
O	−0.010	0.0	−0.002	−0.016	−0.016
H_{HB}	0.004	−0.003	−0.002	0.011	0.011
H_{NB}	−0.002	−0.002	−0.001	0.006	0.007

[a] All shifts evaluated with respect to the charges observed in an uncomplexed water monomer. H_{HB}: H-bonded or π-bonded hydrogen of water. H_{NB}: the remaining hydrogen. See Figure 12 for details of the conformers. Taken from ref 405.

p-difluorobenzene, the OH red shifts seem to be more representative of a σ-type of interaction with the covalently bound fluorine.[443] Interesting, however, are the red shifts associated with the ClFBz−MeOH interaction. The π-bonded conformer displays no red shifts, and this is in excellent agreement with what is observed in experiments.[444]

The focus of most theoretical calculations and experimental observations until now has been on the frequencies of the OH mode. It is, therefore, interesting to examine whether any of the frequencies of the π-system can serve as sensitive indicators of the π−H interaction. In the matrix-isolation studies of the Et−(H_2O), Et−$(H_2O)_2$, and Bz−H_2O complexes, Engdahl and Nelander showed that the IR-active out-of-plane bending modes of both Et and Bz exhibit blue shifts.[372,375] These blue shifts were employed to evaluate the interaction energies of these complexes. However, calculations by us on a large number of complexes seem to indicate that these blue shifts are sensitive indicators of the exchange−repulsion rather than the interaction energies.[405,413,414,448]

5.6. Charges

In general, the formation of a conventional H-bond results in subtle shifts in the electron density.[463] Though these shifts are relatively small in magnitude, they can be employed as fingerprints in the identification of such bonds. This electron density is drawn not only from the lone pair of the acceptor molecule participating in the H-bond but from the entire molecule. Consequently, the density rather than being localized over a particular region delocalizes throughout the donor molecule. It can be seen from the Table 9, which lists the NBO charges (evaluated on the MP2 densities), that there are no discernible changes in the charges on the atoms of the water molecule after formation of the π−H bond in either the Et−H_2O, Tol−H_2O, or Bz−H_2O complexes. The σ-type of interaction in FBz−H_2O and DFBz−H_2O, however, leads to significant changes in the charges. One would like to see if any discernible differences could be observed in the charge distributions of a π−H bond and a normal H-bond when both of them are present in the same system. In Table 10 the shifts in the MP2/aug-cc-pVDZ evaluated NBO charges of all the hydrogens and oxygens of the acceptor and donor water molecules as a result of complexation with the π-system are listed. It can be seen that in both Tol−$(H_2O)_2$ and Bz−$(H_2O)_2$ complexes (which exhibit a π-type of interaction) there is little difference in the charges of acceptor oxygen O_1 as compared to O_2 in $(H_2O)_2$. This is despite the involvement of one of its hydrogens in the formation of a π−H bond. On the other hand, in complexes FBz−$(H_2O)_2$ and DFBz−$(H_2O)_2$, the formation of H-bond with the fluorine of FBz and DFBz results in a significant increase in the negative charge of water oxygen O_1. Thus, it can be said that in contrast to the formation of a σ−H bond, the formation of a π−H bond has no influence on the charges of water oxygen. This contrast also extends to the hydrogen atoms involved in the formation of both σ- and π-bonds. Curiously, Et−$(H_2O)_2$ is an exception to this rule. This possibly might distinguish between the kind of H-bonds formed by an aromatic and olefinic

Table 10. MP2/aug-cc-pVDZ NBO Charge Shifts (au) of the Oxygen and Hydrogen Atoms of the Water Dimer in the Complexes Formed with Ethene (Et), Benzene (Bz), Toluene (Tol), Fluorobenzene (FBz), *p*-Difluorobenzene (DFBz)[a]

atom	Et−$(H_2O)_2$	Tol−$(H_2O)_2$	Bz−$(H_2O)_2$	FBz−$(H_2O)_2$	DFBz−$(H_2O)_2$
$O_1(W_1)$	−0.013	0.001	0.001	−0.013	−0.013
$O_2(W)$	−0.008	−0.010	−0.009	−0.007	−0.008
$H(W_1)$	0.005	0.0	−0.001	0.009	0.009
$H_{NB}(W_1)$	−0.003	−0.002	−0.002	−0.001	0.0
$H_2(W_2)$	0.004	0.005	0.004	0.009	0.009
$H_{NB}(W_2)$	0.006	0.005	0.004	0.007	0.009

[a] All shifts evaluated with respect to the charges observed in an uncomplexed water dimer. See Figure 13 for details of the water molecules. Taken from ref 414. O_1: oxygen attached to the π or σ H-bonded hydrogen., O_2: donor oxygen. H_{NB}: free hydrogens in the water dimer. H: π or σ H-bonded hydrogen. H_2: donor hydrogen.

Table 11. AIM Estimated H-Bond Energies of the Water Dimer Complexes[a]

atom	$(H_2O)_2$	Et−$(H_2O)_2$	Tol−$(H_2O)_2$	Bz−$(H_2O)_2$	FBz−$(H_2O)_2$	DFBz−$(H_2O)_2$
MP2/6-31+G*						
$W_1.W_2$	−7.64	−8.05	−8.42	−8.02	−8.50	−8.50
chrom.W_1		−2.27	−2.19	−2.05	−6.50	−6.18
chrom.W_2		−2.30	−2.31	−1.22	−4.06	−4.37
			−1.05			
MP2/aug-cc-pVDZ						
$W_1.W_2$	−5.54	−6.02	−6.60	−6.13	−6.77	−6.79
chrom.W_1		−2.18	−2.33	−2.19	−5.13	−4.94
chrom.W_2		−1.76	−2.08	−1.28	−3.30	−3.53
			−1.15			

[a] All energies are in units of kcal/mol. See Figure 13 for details of the water molecules. Taken from ref 414.

π-systems. In all the complexes investigated (irrespective of the fact that they exhibit a π- or σ-type of interaction), there is a significant increase in the negative charge of the donor oxygen O_2.

The "atoms in molecules" (AIM) method has extensively been employed to analyze hydrogen bonds[89−91] and weak van der Waals interactions. One of the advantages of the AIM method is that one gets an idea of changes in the electron density distribution as a result of either bond formation or complex formation. It should be noted that in cases of weak van der Waals complexes, these changes may not contribute to the total interaction energy. Recently Abramov proposed the evaluation of the local electronic kinetic energy ($G(r)$) from the experimental electron density distribution ($\rho(r)$).[464] This proposal has further been extended by Espinosa et al.[465] to the evaluation of H-bond strengths using a correlation between the local electronic kinetic energy and the local electronic potential energy. The H-bond strengths of some of the complexes of the water dimer with various π-systems, evaluated using the methodology of Espinosa, are given in Table 11.[414] One readily notices that the numbers reveal some interesting features of the electron density distributions. It can be seen that compared to the isolated $(H_2O)_2$, there is an increased electron density between the two water molecules in the complexed state. This increased electron density translates into a higher potential energy and hence the greater strength of the water H-bond. These data imply that in the presence of a π-system, the H-bond strength of the two water molecules increases dramatically. It would be interesting to extend these observations to explain the experimental fact that Tol, FBz, and DFBz are more immiscible in water than Bz. Results from studies on the corresponding methanol clusters might help explain the miscibility of these π-systems in methanol and their immiscibility in water.

What one learns from these theoretical investigations of these complexes of water and methanol clusters with different π-systems is the role of individual interaction components in governing the geometry and interaction energy. Another aspect which also merits mention is that the increasing size of the water or methanol cluster can favor geometries which are otherwise disfavored for the small clusters. It is interesting to observe the differences exhibited by the fluorinated benzenes regarding their interaction with different systems.

6. π-Complexes with Lewis Acids

A number of Lewis acids are extensively employed as catalysts in a number of organic reactions involving π-systems. Prominent among them are the hydrogen halides and the trihalides of aluminum and boron. There have been very few reports either experimentally or theoretically on whether the interactions of these Lewis acids with the different π-systems involved in various organic reaction has any influence on the observed reaction rates. This is because the role of the Lewis acid was perceived to be only restricted to the generation of a precursor (for example, an electrophile in electrophilic aromatic substitution reactions) which then subsequently interacts with the π-system. However, on a parallel front it has been known for quite some time that molecules containing π-electrons interact with Lewis acids to form weak "donor−acceptor" complexes in solution or strongly bound organometallic compounds.[466]

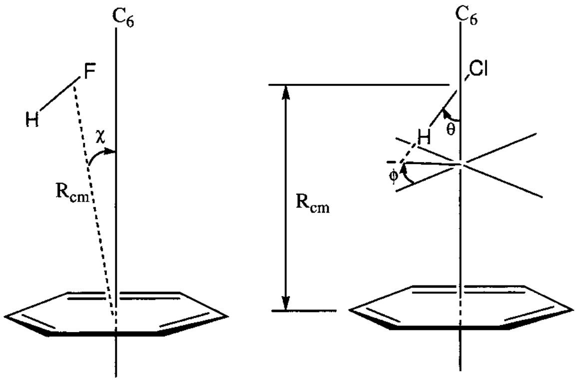


Figure 22. Structures obtained from the rotational spectra of the Bz−HF and Bz−HCl complexes. Note the difference in the position of the center-of-mass of HF and HCl in these complexes. (Reprinted with permission from refs 469 and 472. Copyright 1983, American Institute of Physics and American Chemical Society, respectively.)

6.1. Literature Overview

A number of experimental and theoretical studies exist on the interaction of the hydrogen halides with different π-systems. In the early 1980s, Flygare and co-workers carried out a series of studies on the complexes of HCl and HF with ethyne, ethene, and benzene using microwave spectroscopy.[467−471] It emerges from their experiments that both ethyne and ethene behave as proton acceptors with the acidic hydrogen seeking the high electron density at the centers of the carbon−carbon bonds. Thus, the interactions of ethyne with the hydrogen halides are very different.[369] The experimental data seem to suggest that the Bz−HCl and Bz−HF complexes display very different characteristics regarding the observed geometry.[466,472] In the case of Bz−HCl, the HCl center-of-mass is positioned on the benzene C_6 axis with the orientation of the HCl axis being described by the angles ϕ and θ (Figure 22). The authors indicate that the intermolecular potential is nearly isotropic in ϕ for any arbitrary θ. The Bz−HF complex is different from the Bz−HCl complex in the context of the position of the center-of-mass of HF.[472] It can be seen from Figure 22 that the HF and the benzene C_6 axis are located on the cones about the center-of-mass line. As χ approaches zero, the center-of-mass line will become nearly coincident with the C_6 axis. An aspect which merits attention is the location of the acidic hydrogen in the case of the Bz−HF and Bz−HCl complexes. In both the Bz−HF and Bz−HCl complexes, the acidic hydrogen is directed toward either the ring or one of the benzene carbon atoms, with the latter tendency being more pronounced in the case of Bz−HF. The emphasis of the resonance-enhanced multiphoton ionization (REMPI) study of the Bz−HCl and related complexes was on evaluating the interaction energies.[473] Thus, the interaction energy ($-D_0$) of the Bz−HCl complex is in the range from −1.8 to −3.8 kcal/mol.[473] Replacement of the hydrogen of the HCl molecule by a methyl group leads to a decrease in the interaction energy of the Bz−$\mathrm{CH_3}$ Cl complex to ca. −1.5 to −3.4 kcal/mol.[474] Walters et al. using the photoionization technique deduced the interaction energy ($-D_0$) of the Bz−HCl complex to be in the range −4.79 ± 0.12 kcal/mol.[475] However, there have been no experimental reports of the interaction energies of the Bz−HF complex to date. Using vibrational predissociation, the interaction energies of the Ey−HCl and Ey−HF complexes were accurately estimated by Miller and co-workers.[476,477] The focus of a recent experimental and theoretical study has been on the ab initio assignment of the experimentally obtained vibrational frequencies.[478] An infrared spectroscopic study of the Bz−HF complex also merits mention in this regard.[479] It is of interest to mention a microwave study of the interaction of HCN with benzene in the course of our discussion on interactions of hydrogen halides with π-systems.[480] This study indicates that the Bz−HCN complex has very similar properties to the Bz−HF and Bz−HCl complexes.

On the theoretical front, there have been a large number of studies on the interactions of these hydrogen halides with different π-systems. Since electrostatic interactions dominate the interaction energy of these complexes, it might be expected that calculations at the Hartree−Fock level would be quite successful in the prediction of both the geometries and energies of these complexes. While this is true for the geometries of the complexes, the calculated interaction energies show wide variations with the kind of basis set employed. As for the interaction of Ey−HF, the calculated interaction energies vary from −1.0 to −4.5 kcal/mol and for Ey−HCl from −1.2 to −2.8 kcal/mol. The earliest estimate of the hydrogen-bond energy of Ey−HF by Del Bene indicated a weak interaction energy (ΔE_e^{N}) of −1 kcal/mol.[469] The use of a larger basis set by Kollman increased the interaction energy (ΔE_e^{N}) to −3.2 kcal/mol.[481] Pople and co-workers did some extensive studies at the MP2 level which included geometry optimizations to the equilibrium structure and obtained interaction energies (ΔE_e^{N}) varying from −3.9 to −4.5 kcal/mol.[482] Using a large basis set at the MP2 level, the interaction energy (ΔE_e^{N}) of Ey−HF was estimated to be −3.3 kcal/mol, which is in good agreement with the recent experimentally determined interaction energy of −3.11 kcal/mol.[476,482] It is to be, however, noted that the calculated interaction energy (ΔE_0^{N}) of −3.3 kcal/mol was obtained using the harmonic approximation. On the other hand, in the case of Ey−HCl, none of the theoretical studies until now have been able to match the experimentally determined interaction energy of −2.38 kcal/mol.[477] Thus, the MP2 and MP3 study of Backsay et al. yielded an interaction energy (ΔE_0^{N}) of −2.00 kcal/mol, while the MP4 study of Pople and co-workers obtained a value of −1.9 kcal/mol.[482,487,488] In the case of the larger systems, calculations of Sapse and Jain probed the interactions of HF with both Bz and phenylethyne at the Hartree−Fock level.[494] On the basis of single-point calculations, which were carried out at the MP2 level on the C_{6v} conformers of both Bz−HF and Bz−HCl, Bredas et al. and Cheney et al. inferred that the interaction of HF with Bz is stronger than that of HCl with Bz.[188,189] A latter theoretical study of Bredas and Street on different conformers of Bz−HF [(a) HF oriented along the C_{6v} axis of benzene;

(b) fluorine on the C_6 axis with the acid hydrogen pointing toward a benzene carbon−carbon bond; (c) HF on top of the midpoint of a benzene carbon−carbon bond; (d) HF on top of a benzene carbon atom] predicted that the C_{6v} conformer is the most stable configuration of the Bz−HF complex.[495] However, some of the shortcomings of this study are that the basis sets employed in this study do not include diffuse functions and the interaction energy is neither corrected for BSSE or ZPVE. When these are taken into account in a latter study by Tarakeshwar et al., one observes that the minimal energy conformer is one in which the fluorine atom lies on the C_6 axis with the acid hydrogen pointing toward a benzene carbon−carbon bond.[496] An interesting observation which emerges from this study is that the Bz−HCl interaction is stronger than the Bz−HF interaction.[496] This is in sharp contrast to what is observed in the case of Ey−HF and Ey−HCl. Two recent studies have concentrated on two different aspects of the interaction of the hydrogen halides with these π-systems. Thus, the differences in the interactions of these π-systems when HF is substituted by LiF is the focus of one study.[497] The other study investigated the applicability of DFT methods in the description of these complexes.[498]

There are very few reports on the interactions of either the boron trihalides or aluminum trihalides with different π-systems. Thus, van der Veken and co-workers evaluated the enthalpies of the interaction of boron trifluoride with double-bonded systems such as ethene and propene and triple-bonded systems such as ethyne and propyne using IR spectroscopy.[499,500] The enthalpies were also evaluated theoretically at the MP2/6-31+G* level and compared to the experimental quantities. A detailed vibrational analysis was also carried out on the resulting complexes.[499,500] Fau and Frenking recently compared the interactions of borane with dihydrogen, ethyne, and ethene using Bader's AIM methodology.[501] The interaction of benzene and ethene with both the boron and aluminum trihalides was the focus of some very recent theoretical investigations of Tarakeshwar et al.[502−504]

6.2. Theoretical Studies

There are very few theoretical studies which have compared the interactions of these hydrogen halides with different π-systems. Recently, the interactions of HF with ethyne, ethene, and benzene were investigated at the MP2 level using the 6-31++G** basis set.[497] The interaction energies (ΔE_e^B) seem to indicate that HF is most strongly bound to ethene (−3.59 kcal/mol), followed by ethyne (−3.29 kcal/mol) and benzene (−3.21 kcal/mol). However, the ZPVE corrections dramatically alter the relative stabilities. Thus, calculations carried out at the MP2/aug-cc-pVDZ level reveal that after BSSE and ZPVE corrections, the Bz−HF (−2.67 kcal/mol) interaction is stronger than the Et−HF (−2.35 kcal/mol) interaction.[497]

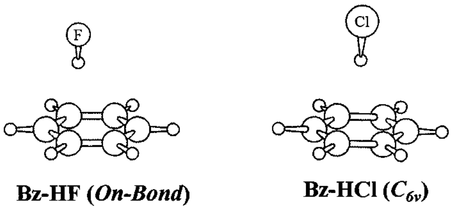


Figure 23. Minimum energy conformers of the Bz−HF and Bz−HCl complexes obtained at the MP2/6-311++G** level.

Table 12. Calculated Binding Energies, Selected Geometrical Parameters of and Conformers of the Bz−HF and Bz−HCl Complexes[a]

	MP2/6-31+G*			MP2/6-311++G(3df,2p)[b]		
	Bz−HF		Bz−HCl	Bz−HF		Bz−HCl
	on-bond	C_{6v}	C_{6v}	on-bond	C_{6v}	C_{6v}
$-\Delta E_e^B$	3.44	3.20	2.55	4.15	4.08	4.33
$-\Delta E_0^B$	1.88	1.47	1.52	2.56	2.30	3.30
$-\Delta E_e$	4.53	4.31	4.03	5.14	5.04	5.52
$-\Delta E_0$	2.97	2.58	3.00	3.55	3.26	4.49
$-\Delta E_{cor}$	2.68	2.69	4.48	3.33	3.18	5.90
$-\Delta E_{es}$	10.22	11.36	6.36	8.33	8.69	4.99
$R_{H-\Phi}$	2.375	2.250	2.330	(2.330)	(2.302)	(2.306)
$R_{X-\Phi}$	3.277	3.196	3.615	(3.236)	(3.223)	(3.584)
R_{H-X}	0.948	0.946	1.285	(0.921)	(0.920)	(1.278)

[a] All energies are in kcal/mol; distances are in Å. ΔE_e^B and ΔE_e are the 100% and 50% BSSE-corrected interaction energies, respectively. ΔE_0^B and ΔE_0 are the ZPE-corrected ΔE_e^B and ΔE_e. The frequencies for ZPE correction were evaluated at the MP2/6-31+G* level. The electron correlation energy ΔE_{cor} is the value of the E_e (MP2) subtracted by E_e (HF) at the MP2 optimized geometry. ΔE_{es} is the electrostatic (charge−charge) interaction energy evaluated using NBO charges. $R_{H-\Phi}$ and $R_{X-\Phi}$ are the distances from the benzene center of mass to the hydrogen and halide atom, respectively. R_{H-X} is the hydrogen halide distance. See Figure 23 for details of the conformers. Taken from ref 496. [b] MP2/6-311++G(3df,2p)/MP2/6-311++G**.

The calculations carried out at the MP2/6-311++G** level on the Bz−HF and Bz−HCl complexes reveal the differences which result from changes in the kind of hydrogen halide interacting with the π-system. Thus, one obtains a C_s structure as the minimum in the case of the Bz−HF complex (Figure 23).[496] In this structure, the hydrogen of HF points to the midpoint of a C−C bond. On the other hand, only a single minimum possessing a C_{6v} symmetry is observed in the case of Bz−HCl.[496] While the calculated geometries are in agreement with the experimentally determined numbers, what is more interesting are the interaction energies of these complexes. At the MP2/6-31+G* level, the calculations indicate that the Bz−HF interaction is stronger than the Bz−HCl interaction. However, when one employs the 6-311++G(3df,2p) basis set, the Bz−HCl interaction becomes stronger than the Bz−HF interaction. It can be seen from the Table 12 that while electrostatic energies dominate the Bz−HF interaction, there is nearly an equal contribution from both electrostatic and dispersive energies in the case of Bz−HCl. Thus, the choice of the basis set plays a crucial role in determining the dispersive contribution and hence the interaction energy of the complex.

In the case of the interactions of the boron and aluminum trihalides with ethene, the staggered C_s conformers wherein one of the Y−X (X = H,F,Cl) bonds is orthogonal to the C−C double bond of the

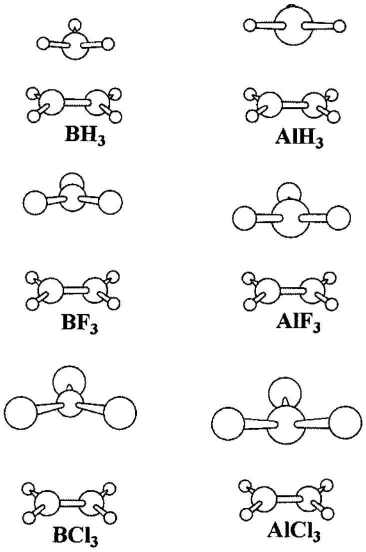


Figure 24. Minimum energy conformers of Et−BX_3 and Et−AlX_3 (X = H, F, Cl) obtained at the MP2/6-311++G** level.

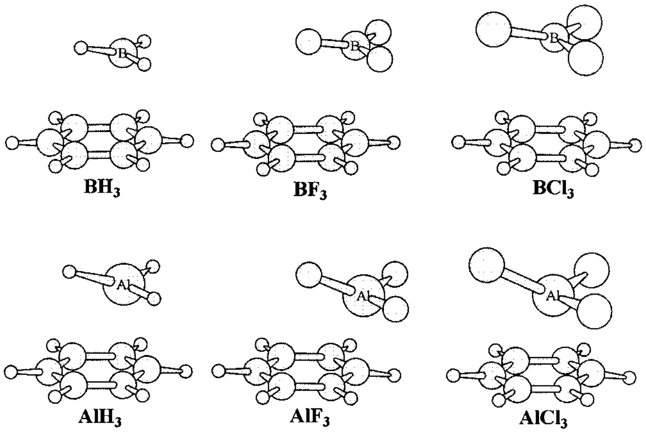


Figure 25. Minimum energy conformers of the Bz−BX_3 and Bz−AlX_3 (X = H, F, Cl) obtained at the MP2/6-311++G** level.

ethene are the minimum energy structures (Figure 24). In the case of their complexes with benzene, the B or Al atom is directly placed over one of the carbon atoms and is extremely close to the benzene π-plane as can be seen from Figure 25. Conformers in which the Al or B atom is directly placed over the C_{6v} axis of benzene are all second-order saddle-point structures. Interesting is the intermolecular distance separating the YX_3 moiety from the benzene carbon in the minimum energy structures obtained at the MP2/6-311++G** level. In the case of the boron trihalides, the distances range from 2.456 to 3.223 Å with the Bz−H_2O complex exhibiting the largest separation. In sharp contrast, the benzene complexes of the aluminum trihalides exhibit very short intermolecular distances (2.324−2.571 Å) and the Bz−H_2O complex exhibits the smallest separation.

A major difference in the binding of benzene or ethene with BX_3 and AlX_3 is that in the AlX_3 complexes, electrostatic interactions have a dominant contribution to the interaction energy, while in the BX_3 complexes, dispersive interactions have a dominant role. The various energies are plotted in a histogram format in Figure 26. One observes that the AlX_3 complexes conform to the general behavior of donor−acceptor complexes (i.e., electrostatic interactions dominate the interaction energy) with some notable exceptions. The AlX_3 complexes, in general, with the exception of the Et−AlH_3 complex, are characterized by large interaction energies (ΔE_0) in the range of (−8 to −17 kcal/mol). This is in contrast to what is observed in the case of the BX_3 complexes (−3.3 to −5.9 kcal/mol). Of particular interest are the energies exhibited by the BF_3 and AlF_3 complexes. While the ethene and benzene complexes of BF_3 exhibit the lowest interaction energies among the boron-containing complexes, the corresponding AlF_3 complexes exhibit the largest interaction energies.

A question which is of interest in the context of the geometries and interaction energies of the Bz and Et complexes of these Lewis acids is on whether these interactions lead to any changes in the charge characteristics of the π-system. This question assumes particular significance due to the widespread usage of Lewis acids as catalysts in electrophilic aromatic substitution reactions. Figure 27 reveals that the carbon atom of Bz which lies directly below the Lewis acid exhibits a dramatic increase in the negative charge when compared to the remaining five carbon atoms. A simultaneous increase in the positive charge on the hydrogen atom attached to this carbon can also be seen. This increase in the negative charge (or nucleophilicity) of the carbon atom could ease an electrophilic attack on this particular benzene carbon as a result of a significant lowering in the activation energy. Furthermore, the increase in the positive charge on the hydrogen attached to this carbon would facilitate its departure after an attack by an electrophile.

It is of interest to note that these charge effects are not limited to these Lewis acids. Similar effects are also observed in the interaction of different electrophiles (cations) with Bz.

7. Summary and Outlook

In this review, we have discussed the interactions of a number of π-systems with different ligands ranging from the simplest rare-gas atom to the more complex water or methanol clusters. Some of the salient results obtained from theoretical calculations of these complexes are outlined below. (i) The characteristics of the interaction energies of these π-complexes are dependent on both the nature of the ligand and the π-system. Thus, when the ligand is a metal cation, electrostatic interactions dominate the interaction energy. Dispersive interactions dominate when the ligand is either a rare-gas atom or a nonpolar molecule (gas dimers, hydrocarbons). A combination of electrostatic and dispersive interactions govern the interaction energy when the ligand is polar (water or methanol clusters, Lewis acids). In all cases, the repulsive interactions have a vital role in governing the observed geometry. (ii) When an electron-donating substituent is present on the aromatic ring, the resulting π-complexes formed have enhanced interaction energies compared to benzene. This enhancement is due to an increase in both dispersive or

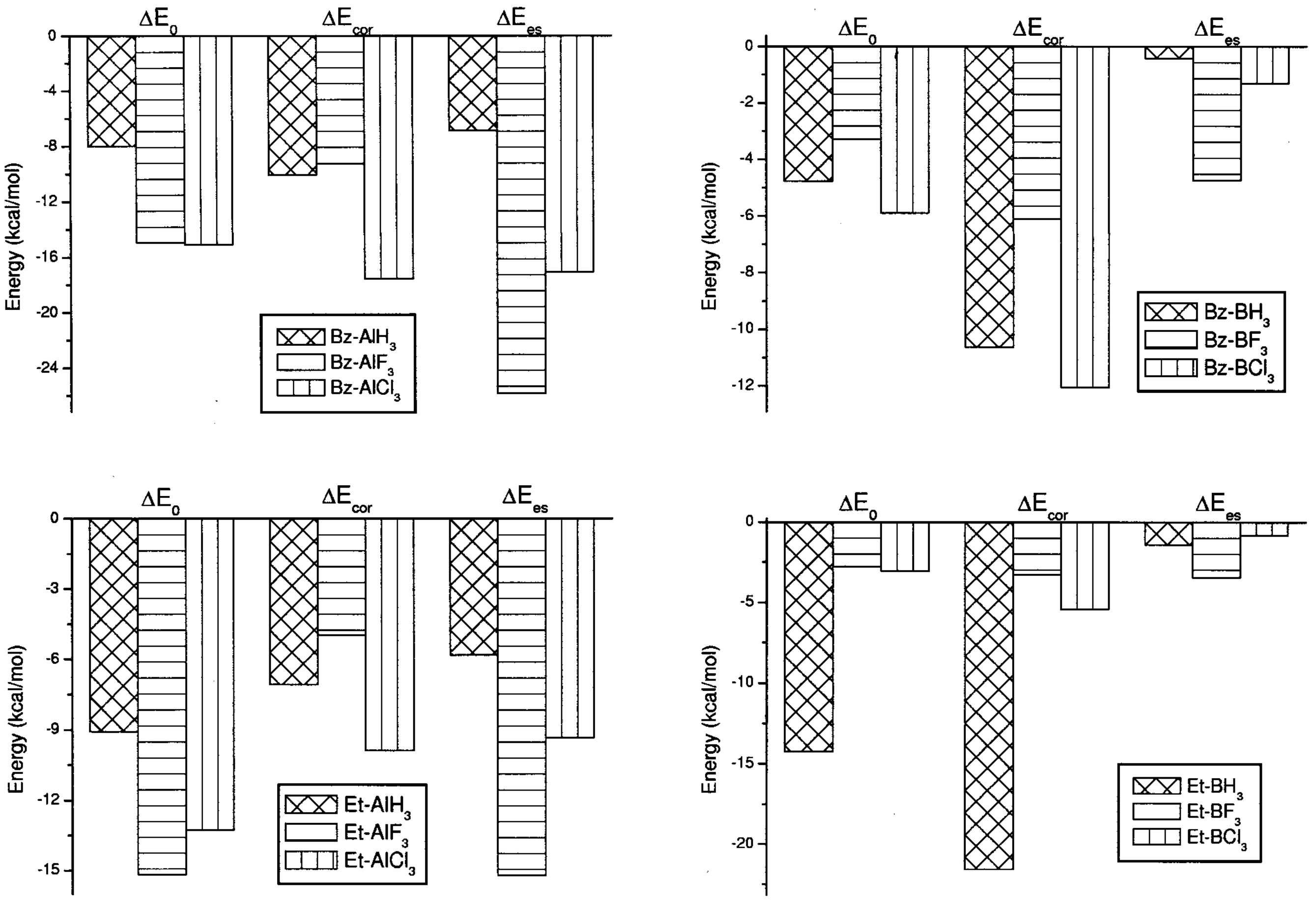


Figure 26. Comparison of the interaction, electrostatic, and correlation energies of the lowest energy conformers of the Et/Bz$-$BX$_3$ and Et/Bz$-$AlX$_3$ complexes obtained at the MP2/6-311++G(3df,2p) level.

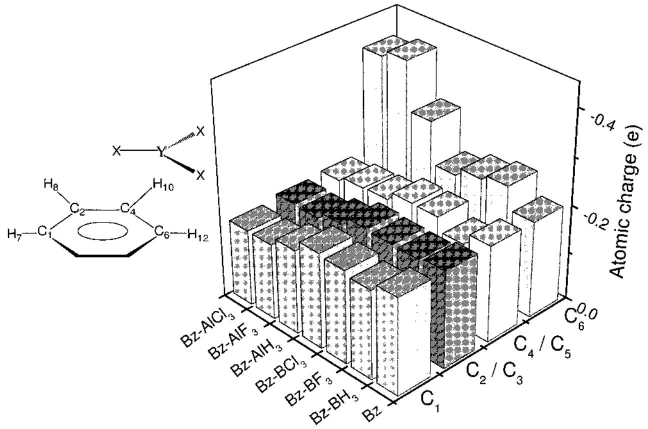


Figure 27. MP2/6-311++G(3df,2p) NBO charges of different carbon atoms of benzene in the Bz$-$AlX$_3$ complexes.

electrostatic interactions. On the other hand, the geometries of complexes formed with aromatic rings having electronegative substituents is extremely dependent on the characteristics of the interaction energy. Thus, when the interaction energy is dominated by dispersive interactions, a π-type of complex is formed. When electrostatic energies predominate the interaction energy, a σ-type of complex involving the electronegative substituent is formed. When the ligand is a water or methanol cluster, the size of the cluster interaction with the π-system has a crucial influence on the nature of the resulting structure (σ or π). (iii) While the formation of a conventional H-bond is governed by electrostatic interactions, dispersive interactions play an important role in the formation of a $\pi$$-$H-bond.

The results obtained from calculations carried out using DFT methods seem to indicate that the present functionals are not suitably parametrized to describe the long-range dispersive interactions prevalent in these weakly bound complexes of π-systems.

Some of the species whose interactions with these π-systems that have not been discussed in these review are sulfur-containing molecules and anions. There have been few experimental and theoretical studies of the interactions of sulfur-containing molecules with π-systems.[505-509] Given the role of sulfur-containing amino acids in governing the structure of proteins and their presence in a number of active sites in enzymes, it would be worthwhile to examine both the energetic extent and the nature of sulfur-containing molecules with π-systems.

The interactions of electron-rich anions with various π-systems are also of interest, given the importance of electron solvation and electron-transfer phenomena in both biology and chemistry.[510-514] The recent investigations of electrons solvated in water clusters have yielded a number of surprises regarding the structures (Figure 28) and properties of these systems.[364,368] A beginning has already been made in that direction given the recent spate of articles on the structure and properties of anionic π-complexes.[515-519] More details on some of these systems

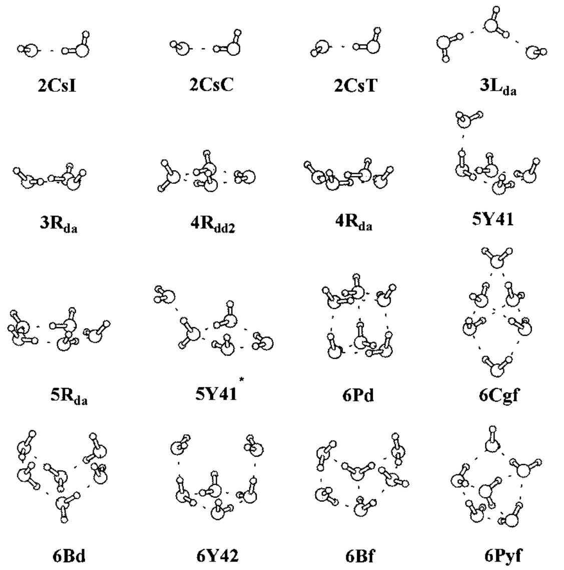


Figure 28. Low-lying energy structures obtained for different sizes of the e^-–water clusters.

can be obtained from the review of Schermann in this issue.

It can also be observed from this review that the number of investigations on the interactions of methanol with various π-systems is also sparse. A paradox which has confronted a number of chemists since ages has been the solubility of benzene in methanol and its insolubility in water. It would be of interest if an explanation could be obtained from investigations of complexes of these π-systems with methanol clusters.

Much effort has gone in the recent past in applying the knowledge gained from theoretical investigations of various types of interactions in the design of functional molecular systems. In recent years, we focused our attention on the interactions of π-systems with biologically and chemically important hosts/guests and their role in the active sites of enzymes.[520–521] The preliminary results obtained on related systems seem to indicate that this area could be a promising field of research soon.

8. Abbreviations

AIM	atoms in molecules
B3LYP	Becke's three-parameter hybrid functional using the Lee, Yang, and Parr correlation functional
BSIE	basis set incompletion error
BSSE	basis set superposition error
CCSD	coupled-cluster singles and doubles substitution
DFT	density functional theory
CCSD(T)	coupled-cluster singles and doubles substitution with triples excitation
HF	Hartree–Fock, hydrogen fluoride
ILSRS	ionization-loss simulated Raman spectroscopy
IR	infrared
MIDI	Huzinaga's 21 split valence basis set
MP2	second-order Møller–Plesset perturbation theory
NBO	natural bond orbital
RCS	rotational coherence spectroscopy
SM	supermolecular
SAPT	symmetry adapted perturbation theory
TOFMS	time-of-flight mass spectroscopy
ZPVE	zero-point vibrational energy

9. Acknowledgments

This work was supported by the Korean Ministry of Science and Technology under the Creative Research Initiatives Program. We thank Professors B. Brutschy, P. Hobza, N. Mikami, and T. S. Zwier for helpful discussions in the course of writing this review. We thank Professor K. Szalewicz for helpful suggestions in making SAPT run for the large systems reported in this review. We also thank the referees for their critical comments on the original version of this review.

10. Note Added in Proof

In the discussion of competition between cation-π, cation-solvent, and hydrogen bond interactions, the work of Lisy and coworkers,[522] merits mention.

11. References

(1) Müller-Dethlefs, K.; Hobza, P. *Chem. Rev.* **2000**, *100,* 143.
(2) Hobza, P.; Šponer, J. *Chem. Rev.* **1999**, *99*, 3247.
(3) Alkorta, I.; Rozas, I.; Elguero, J. *Chem. Soc. Rev.* **1998**, 163.
(4) Ebata, T.; Fujii, A.; Mikami, N. *Int. Rev. Phys. Chem.* **1998**, *17*, 331.
(5) Saigusa, H.; Lim, E. C. *Acc. Chem. Res.* **1996**, *29*, 171.
(6) Lester, M. I. *Adv. Chem. Phys.* **1996**, *96*, 51.
(7) Sun. S.; Bernstein, E. R. *J. Phys. Chem.* **1996**, *100*, 13348.
(8) Bernstein, E. R. *Annu. Rev. Phys. Chem.* **1995**, *46*, 197.
(9) Hobza, P.; Selzle, H. L.; Schlag, E. W. *Chem. Rev.* **1994**, *94*, 1767.
(10) Felker, P. M.; Maxton, P. M.; Schaeffer, M. W. *Chem. Rev.* **1994**, *94*, 1787.
(11) Neusser, H. J.; Krause, H. *Chem. Rev.* **1994**, *94*, 1829.
(12) Müller-Dethlefs, K.; Dopfer, O.; Wright, T. G. *Chem. Rev.* **1994**, *94*, 1845.
(13) Klemperer, W. *Science* **1992**, *257*, 887.
(14) Brutschy, B. *Chem. Rev.* **1992**, *92*, 1567.
(15) Bačić, Z.; Miller, R. E. *J. Phys. Chem.* **1996**, *100*, 12945.
(16) Stone, A. J. *The Theory of Intermolecular Forces*; Clarendon Press: Oxford, 1996.
(17) Karlström, G.; Linse, P.; Wallqvist, A.; Jönsson, B. *J. Am. Chem. Soc.* **1983**, *105*, 3777. Åstrand, P.-O.; Wallqvist, A.; Karlström, G. *J. Chem. Phys.* **1994**, *100*, 1262. Åstrand, P.-O.; Linse, P.; Karlström, G. *Chem. Phys.* **1995**, *191*, 195.
(18) Jorgensen, W. L.; Briggs, J. M.; Contreras, M. L. *J. Phys. Chem.* **1990**, *94*, 1683. Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.
(19) Sorenson, J. M.; Gregory, J. K.; Clary, D. C. *J. Chem. Phys.* **1997**, *106*, 849.
(20) Dykstra, C. E. *Chem. Rev.* **1993**, *93*, 2339. Dykstra, C. E. *J. Am. Chem. Soc.* **1989**, *111*, 6168; **1990**, *112*, 7540.
(21) Stone, A. J. *Chem. Phys. Lett.* **1981**, *83*, 233. Stone, A. J.; Alderton, M. *Mol. Phys.* **1985**, *56*, 1047.
(22) Popelier, P. L. A.; Stone, A. J.; Wales, D. J. *Faraday Discuss. Chem. Soc.* **1994**, *97*, 243.
(23) Claverie, P. In *Intermolecular Interactions from Diatomics to Biopolymers*; Pullman, B., Ed.; Wiley: New York, 1978.
(24) Hess, O.; Caffarel, M.; Langlet, J.; Caillet, J.; Huiszoon, C.; Claverie, P. In *Proceedings of the 44th International Meeting Modelling of Molecular Structures and Properties in Physical Chemistry and Biophysics*, Nancy, France, Sept 11–15, 1989; Rivail, J. L., Ed.; Elsevier: Amsterdam, 1990.
(25) Vigne-Maeder, F.; Claverie, P. *J. Chem. Phys.* **1988**, *88*, 4934.
(26) Hess, O.; Caffarel, M.; Huiszoon, C.; Claverie, P. *J. Chem. Phys.* **1990**, *92*, 6049.
(27) Jeziorski, B.; Moszynski, R.; Szalewicz, K. *Chem. Rev.* **1994**, *94*, 1887.
(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; 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.; Cami, 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.5; Gaussian Inc.: Pittsburgh, PA, 1998.

(29) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(30) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989** *162*, 165. Ahlrichs, R.; Arnim, M. v. In *Methods and Techniques in Computational Chemistry: METECC-95*; Clementi, E., Corongiu, G., Eds.; STEF: Cagliari, 1995.

(31) *Jaguar*, v 3.5; Schrödinger, Inc.: Portland, OR, 1998.

(32) Stanton, J. F.; Gauss, J.; Watss, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1992**, *26*, 879.

(33) MOLPRO is a package of programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Petersen, R. Pitzer, A. J. Stone,P. R. Taylor, and R. Lindh.

(34) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(35) Shavitt, I. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed; Plenum Press: New York, 1977. Siegbahn, P. E. M. In *Methods in Computational Molecular Physics*; Diercksen, G. H. F., Wilson, S., Ed.; D. Reidel: Dordrecht, 1983.

(36) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545. Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35. Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 516. Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III *J. Chem. Phys.* **1988**, *89*, 7382. Scuseria, G. E.; Schaefer, H. F., III *J. Chem. Phys.* **1989**, *90*, 3700.

(37) Crawford, T. D.; Schaefer, H. F., III *Rev. Comput. Chem.* **2000**, *14*, 33.

(38) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864. Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.

(39) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.

(40) *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J. W., Eds.; Springer-Verlag: New York, 1991.

(41) Chalasiński, G.; Szczęśniak, M. M. *Chem. Rev.* **1994**, *94*, 1723.

(42) Szalewicz, K.; Jeziorski, B. In *Molecular Interactions−From van der Waals to Strongly Bound Complexes*; Scheiner, S., Ed.; Wiley: New York, 1997; p 3.

(43) Jeziorski, B.; Moszynski, R.; Ratkiewicz, A.; Rybak, S.; Szalewicz, K.; Williams, H. L. In *Methods and Techniques in Computational Chemistry: METECC-94*; Clementi, E., Ed.; STEF: Cagliari, 1993; Vol. B (Medium Sized Systems), pp 79−129.

(44) Williams, H. L.; Szalewicz, K.; Jeziorski, B.; Moszynski, R.; Rybak, S. *J. Chem. Phys.* **1993**, *98*, 1279.

(45) Moszynski, R.; Wormer, P. E. S.; Jeziorski, B.; van der Avoird, A. *J. Chem. Phys.* **1994**, *101*, 2811.

(46) Moszynski, R.; Korona, T.; Wormer, P. E. S.; van der Avoird, A. *J. Chem. Phys.* **1995**, *103*, 321.

(47) Lotrich, V. F.; Williams, H. L.; Szalewicz, K.; Jeziorski, B.; Moszynski, R.; Wormer, P. E. S.; van der Avoird, A. *J. Chem. Phys.* **1995**, *103*, 6076.

(48) Moszynski, R.; Wormer, P. E. S.; van der Avoird, A. *J. Chem. Phys.* **1995**, *102*, 8385.

(49) Jankowski, P.; Szalewicz, K. *J. Chem. Phys.* **1998**, *108*, 3554.

(50) Szalewicz, K.; Cole, S. J.; Kolos, W.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *89*, 3662.

(51) Mas, E. M.; Szalewicz, K. *J. Chem. Phys.* **1996**, *104*, 7606.

(52) Mas, E. M.; Szalewicz, K.; Bukowski, R.; Jeziorski, B. *J. Chem. Phys.* **1997**, *107*, 4207.

(53) Langlet, J.; Caillet, J.; Caffarel, M. *J. Chem. Phys.* **1995**, *103*, 8043.

(54) Williams, H. L.; Rice, B. M.; Chabalowski, C. F. *J. Phys. Chem. A* **1998**, *102*, 6981.

(55) Turki, N.; Milet, A.; Rahmouni, A.; Ouamerali, O.; Moszynski, R.; Kochanski, E.; Wormer, P. E. S. *J. Chem. Phys.* **1998**, *109*, 7157.

(56) Chandra, A. K.; Nguyen, M. T. *J. Phys. Chem. A.* **1998**, *102*, 6865.

(57) Jagielska, A.; Moszynski, R.; Piela, L. *J. Chem. Phys.* **1999**, *110*, 947.

(58) Bukowski, R.; Sadlej, J.; Jeziorski, B.; Jankowski, P.; Szalewicz, K.; Kucharski, S. A.; Williams, H. L.; Rice, B. M. *J. Chem. Phys.* **1999** *110*, 3785.

(59) Milet, A.; Moszynski, R.; Wormer, P. E. S.; van der Avoird, A. *J. Phys. Chem. A* **1999**, *103*, 6811.

(60) Moszynski, R.; Jeziorski, B.; Ratkiewicz, A.; Rybak, S. *J. Chem. Phys.* **1993**, *99*, 8856. Moszynski, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1994**, *100*, 1312. Moszynski, R.; Jeziorski, B.; Rybak, S.; Szalewicz, K.; Williams, H. L. *J. Chem. Phys.* **1994**, *100*, 5080. Rybak, S.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1991**, *95*, 6576. Moszynski, R.; Cybulski, S. M.; Chalasiński, G. *J. Chem. Phys.* **1994**, *100*, 4998. Moszynski, R.; Korona, T.; Wormer, P. E. S.; van der Avoird, A. *J. Phys. Chem. A* **1997**, *101*, 4690.

(61) Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Chem. Phys.* **1991**, *95*, 391.

(62) Jansen, H. B.; Ros. P. *Chem. Phys. Lett.* **1969**, *3*, 140.

(63) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(64) Cybulski, S. M.; Chalasiński, G. *Chem. Phys. Lett.* **1992**, *197*, 591.

(65) Gutowski, M.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H.; van Duijneveldt, F. B. *J. Chem. Phys.* **1993**, *98*, 4728.

(66) Gutowski, M.; Chalasiński, G. *J. Chem. Phys.* **1993**, *98*, 5540.

(67) Mayer, I.; Valiron, P. *J. Chem. Phys.* **1998**, *109*, 3360.

(68) Simon, S.; Duran, M.; Dannenberg, J. J. *J. Phys. Chem. A* **1999**, *103*, 1640. Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **1996**, *105*, 11024.

(69) Davidson, E. R.; Chakravorty, S. J. *Chem. Phys. Lett.* **1994**, *217*, 48.

(70) Davidson, E. R.; Chakravorty, S. J. *Chem. Phys. Lett.* **1995**, *241*, 146.

(71) Gutowski, M.; Szczeńniak, M.; Chalasiński, G. *Chem. Phys. Lett.* **1995**, *241*, 140.

(72) van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.* **1994**, *94*, 1873.

(73) van Duijneveldt, F. B. In *Molecular Interactions−From van der Waals to Strongly Bound Complexes*; Scheiner, S., Ed.; Wiley: New York, 1997; p 81.

(74) Kim, K. S.; Mhin, B. J.; Choi, U.-S.; Lee, K. *J. Chem. Phys.* **1992**, *97*, 6649.

(75) Kim, J.; Lee, S.; Cho, S. J.; Mhin, B. J.; Kim, K. S. *J. Chem. Phys.* **1995**, *102*, 839.

(76) Kim, J.; Kim, K. S. *J. Chem. Phys.* **1998**, *109*, 5886.

(77) Feller, D. *J. Phys. Chem. A* **1999**, *103*, 7558.

(78) Schütz, M.; Brdarski, S.; Widmark, P.-O.; Lindh, R.; Karlström, G. *J. Chem. Phys.* **1997**, *107*, 4597.

(79) Halkier, A.; Koch, H.; Jørgensen, P.; Christiansen, O.; Beck Nielsen, I. M.; Helgaker, T. *Theor. Chem. Acc.* **1997**, *97*, 150.

(80) Hobza, P.; Bludský, O.; Suhai, S. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3073.

(81) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(82) Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1997**, *398*, 181.

(83) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990. Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893.

(84) Biegler-Koning, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317.

(85) Popelier, P. L. A. *Comput. Phys. Commun.* **1996**, *93*, 212.

(86) Bone, R. G. A.; Bader, R. F. W. *J. Phys. Chem.* **1996**, *100*, 10892.

(87) Tang, T.-H.; Hu, W.-J.; Yan, D.-Y.; Cui, Y.-P. *J. Mol. Struct. (THEOCHEM)* **1991**, *207*, 319.

(88) Popelier, P. L. A. *J. Phys. Chem. A* **1998**, *102*, 1873.

(89) Rozas, I.; Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **1997**, *101*, 9457.

(90) Cubero, E.; Orozco, M.; Luque, F. J. *J. Phys. Chem. A* **1999** *103*, 6054.

(91) Cubero, E.; Orozco, M.; Hobza, P.; Luque, F. J. *J. Phys. Chem. A* **1999** *103* 6394.

(92) Dewar, M. J. S. *J. Chem. Soc.* **1946**, 406.

(93) Morokuma, K. *J. Chem. Phys.* **1971**, 55, 1236.

(94) Watanabe, H.; Iwata, S. *J. Chem. Phys.* **1996**, *105*, 420.

(95) Iwasaki, A.; Fujii, A.; Watanabe, T.; Ebata, T.; Mikami, N. *J. Phys. Chem.* **1996**, *100*, 16053.

(96) Schiefke, A.; Deusen, C.; Jacoby, C.; Gerhards, M.; Schmitt, M.; Kleinermanns, K.; Hering, P. *J. Chem. Phys.* **1995**, *102*, 9197.

(97) Siebrand, W.; Zgierski, M. Z.; Smedarchina, Z. K.; Vener, M.; Kaneti, J. *Chem. Phys. Lett.* **1997**, *266*, 47.

(98) Hobza, P.; Burcl, R.; Špirko, V.; Dopfer, O.; Müller-Dethlefs, K.; Schlag, E. W. *J. Chem. Phys.* **1994**, *101*, 990.

(99) Manyin, Y.; Scheiner, S. *Chem. Phys. Lett.* **1996**, *262*, 567.

(100) Sodupe, M.; Oliva, A.; Bertrán, J. *J. Phys. Chem. A* **1997**, *101*, 9142.

(101) Roth, W.; Schmitt, W.; Jacoby, Ch.; Spangenberg, D.; Janzen, Ch.; Kleinermans, K. *Chem. Phys.* **1998**, *239*, 1.

(102) Fujii, A.; Miyazaki, M.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **1999**, *110*, 11125.

(103) Inauen, A.; Hewel, J.; Leutwyler, S. *J. Chem. Phys.* **1999**, *110*, 1463.

(104) Bach, A.; Leutwyler, S. *Chem. Phys. Lett.* **1999**, *299*, 381.

(105) Bach, A.; Hewel, J.; Leutwyler, S. *J. Phys. Chem. A* **1998**, *102*, 10476.

(106) Chapman, D. M.; Müller-Dethlefs, K. *J. Chem. Phys.* **1999**, *111*, 1955.

(107) Haines, S. R.; Geppert, W. D.; Chapman, D. M.; Watkins, M. J.; Dessent, C. E. H.; Cockett, M. C. R.; Müller-Dethlefs, K. *J. Chem. Phys.* **1998**, *109*, 9244.

(108) Chapman, D. M.; Hompf, F. J.; Müller-Dethlefs, K.; Waterstradt, E.; Hobza, P.; Špirko, V. *Chem. Phys.* **1998**, *239*, 417.

(109) Haines, S. R.; Dessent, C. E. H.; Müller-Dethlefs, K. *J. Chem. Phys.* **1999**, *111*, 1947.
(110) Gerhards, M.; Kleinermans, K. *J. Chem. Phys.* **1995**, *103*, 7392.
(111) Ishikawa, S.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **1999**, *110*, 9504.
(112) Matsuda, Y.; Ebata, T.; Mikami, N. *J. Chem. Phys.* **1999**, *110*, 8397.
(113) Storm, V.; Dreizler, H.; Consalvo, D. *Chem. Phys.* **1998**, *239*, 109.
(114) Spoerel, U.; Stahl, W. *Chem. Phys.* **1998**, *239*, 97.
(115) Caminati, W.; Favero, L. B.; Favero, P. G.; Maris, A.; Melandri, S. *Angew. Chem., Int. Ed.* **1998**, *37*, 792.
(116) Melandri, S.; Sanz, M. E.; Caminati, W.; Favero, P. G.; Kisiel, Z. *J. Am. Chem. Soc.* **1998**, *120*, 11504.
(117) Dolgounitcheva, O.; Zakrzewski, V. G.; Ortiz, J. V. *J. Phys. Chem. A* **1999**, *103*, 7912.
(118) van Mourik, T.; Price, S. L.; Clary, D. C. *J. Phys. Chem. A* **1999**, *103*, 1611.
(119) Leutwyler, S.; Bösiger, J. *Chem. Rev.* **1990**, *90*, 489.
(120) Brupbacher, Th.; Makarewicz, J.; Bauder, A. *J. Chem. Phys.* **1994**, *101*, 9736.
(121) Hobza, P.; Bludsky, O.; Selzle, H.; Schlag, E. *Chem. Phys. Lett.* **1996**, *250*, 402.
(122) Vacek, J.; Hobza, P.; Jortner, J. *J. Phys. Chem. A* **1998**, *102*, 8268.
(123) Lu, W.; Hu, Y.; Yang, S. *J. Chem. Phys.* **1998**, *108*, 12.
(124) Klopper, W.; Lüthi, H. P.; Brupbacher, Th.; Bauder, A. *J. Chem. Phys.* **1994**, *101*, 9747.
(125) Droz, T.; Bürgi, T.; Leutwyler, S. *J. Chem. Phys.* **1995**, *103*, 4035.
(126) Sussmann, R.; Neusser, H. J. *J. Chem. Phys.* **1995**, *102*, 3055.
(127) Vacek, J.; Hobza, P. *J. Phys. Chem.* **1995**, *99*, 17088.
(128) Onda, M.; Bitoh, Y.; Hight-Walker, A. *J. Mol. Struct.* **1997**, *410*, 51.
(129) Sinclair, W. E.; Pratt, D. W. *J. Chem. Phys.* **1996**, *105*, 7942.
(130) Becucci, M.; Pietraperzia, G.; Lakin, N.; Castellucci, E.; Bréchignac, Ph. *Chem. Phys. Lett.* **1996**, *260*, 87.
(131) Consalvo, D.; Storm, V.; Dreizler, H. *Chem. Phys.* **1997**, *228*, 301.
(132) Arunan, E.; Emilsson, T.; Gutowsky, H. S. *J. Chem. Phys.* **1994**, *101*, 861.
(133) Lakin, N. M.; Pietraperzia, G.; Becucci, M.; Castellucci, E.; Coreno, M.; Giardini-Guidoni, A.; van der Avoird, A. *J. Chem. Phys.* **1998**, *108*, 1836.
(134) Coreno, M.; Piccirillo, S.; Giardini-Guidoni, A.; Mele, A.; Palleschi, A.; Bréchignac, Ph.; Parneix, P. *Chem. Phys. Lett.* **1995**, *236*, 580.
(135) Parneix, P.; Amar, F. G.; Bréchignac, Ph. *Chem. Phys.* **1998**, *239*, 121.
(136) Hartmann, M.; Lindinger, A.; Toennies, J. P.; Vilesov, A. F. *Chem. Phys.* **1998**, *239*, 139.
(137) Uridat, D.; Brenner, V.; Dimicoli, I.; Le Calvé, J.; Millié, P.; Mons, M.; Piuzzi, F. *Chem. Phys.* **1998**, *239*, 151.
(138) Caminati, W.; Favero, P. G.; Velino, B. *Chem. Phys.* **1998**, *239*, 223.
(139) Tanaka, D.; Sato, S.; Kimura, K. *Chem. Phys.* **1998**, *239*, 437.
(140) Melandri, S.; Maccaferi, G.; Maris, A.; Millemaggi, A.; Caminati, W.; Favero, P. G. *Chem. Phys. Lett.* **1996**, *261*, 267.
(141) Caminati, W.; Favero, P. G.; Melandri, S.; Meyer, R. *Chem. Phys. Lett.* **1997**, *268*, 393.
(142) Caminati, W.; Millemaggi, A.; Favero, P. G.; Makarewicz, J. *J. Phys. Chem.* **1997**, *101*, 9272.
(143) Caminati, W.; Melandri, S.; Millemaggi, A.; Favero, P. G. *Chem. Phys. Lett.* **1998**, *294*, 377.
(144) Spycher, R.; Hausherr-Primo, L.; Grassi, G.; Bauder, A. *J. Mol. Struct.* **1995**, *351*, 7.
(145) Spycher, R.; Petitprez, D.; Bettens, F.; Bauder, A. *J. Phys. Chem.* **1994**, *98*, 11863.
(146) Wilson, R. J.; Peebles, S. A.; Antolínez, S.; Sanz, M. E.; Kuczkowski, R. L. *J. Phys. Chem. A* **1998**, *102*, 10630.
(147) Koch, H.; Fernández, B.; Christiansen, O. *J. Chem. Phys.* **1998**, *108*, 2784.
(148) Koch, H.; Fernández, B.; Makarewicz, J. *J. Chem. Phys.* **1999**, *111*, 198.
(149) Kraka, E.; Cremer, D.; Spoerel, U.; Merke, I.; Stahl, W.; Dreizler, H. *J. Phys. Chem.* **1995**, *99*, 12466.
(150) Spoerel, U.; Dreizler, H.; Stahl, W.; Kraka, E.; Cremer, D. *J. Phys. Chem.* **1996**, *100*, 14298.
(151) Hobza, P.; Bludský, O.; Selzle, H. L.; Schlag, E. W. *J. Chem. Phys.* **1992**, *97*, 335.
(152) Krause, H.; Neusser, H. J. *J. Chem. Phys.* **1993**, *99*, 6278.
(153) Reidle, E.; van der Avoird, A. *J. Chem. Phys.* **1996**, *104*, 882.
(154) Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Chem. Phys.* **1993**, *99*, 2809.
(155) Su, M.-C.; O, H. K.; Parmenter, C. S. *Chem. Phys.* **1991**, *156*, 261.
(156) Spoerel, U.; Consalvo, D. *Chem. Phys.* **1998**, *49*, 199.
(157) Korter, T. M.; Kupper, J.; Pratt, D. W. *J. Chem. Phys.* **1999**, *111*, 3946.
(158) Abou-Zied, O. K.; Sinha, H. K.; Steer, R. P. *J. Phys. Chem.* **1996**, *100*, 4375.
(159) Bernshtein, V.; Oref, I. *J. Chem. Phys.* **2000**, *112*, 686.
(160) López-Tocón, I.; Otero, J. C.; Becucci, M.; Pietraperzia, G.; Castelucci, E. *Chem. Phys.* **1999**, *249*, 113.
(161) Unpublished results.
(162) Hobza, P.; Bludský, O.; Selzle, H. L.; Schlag, E. W. *J. Chem. Phys.* **1993**, *98*, 6223.
(163) Wesolowski, T. A.; Parisel, O.; Ellinger, Y.; Weber, J. *J. Phys. Chem. A* **1997**, *101*, 7818.
(164) Wesolowski, T. A.; Ellinger, Y.; Weber, J. *J. Chem. Phys.* **1998**, *108*, 6078.
(165) Granucci, G.; Persico, M. *Chem. Phys. Lett.* **1993**, *205*, 331.
(166) Brupbacher, Th.; Bauder, A. *J. Chem. Phys.* **1993**, *99*, 9394.
(167) Hu, Y.; Lu, W.; Yang, S. *J. Chem. Phys.* **1996**, *105*, 5305.
(168) Casero, J. J.; Joens, J. A. *J. Phys. Chem. A* **1999**, *103*, 7136.
(169) Casero, J. J.; Joens, J. A. *J. Phys. Chem. A* **1997**, *101*, 2607.
(170) Gooding, E. A.; Serak, K. R.; Ogilby, P. R. *J. Phys. Chem.* **1991**, *95*, 7868.
(171) Grover, J. R.; Hagenow, G.; Walters, E. A. *J. Chem. Phys.* **1992**, *97*, 628.
(172) Legon, A. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2686.
(173) Su, J. T.; Zewail, A. H. *J. Phys. Chem. A* **1998**, *102*, 4082.
(174) Bernstein, E. R.; Law, K. S.; Schauer, M. *J. Chem. Phys.* **1984**, *80*, 634.
(175) Schauer, M.; Law, K. S.; Bernstein, E. R. *J. Chem. Phys.* **1984**, *81*, 49.
(176) Schauer, M.; Bernstein, E. R. *J. Chem. Phys.* **1985**, *82*, 726.
(177) Schauer, M.; Law, K. S.; Bernstein, E. R. *J. Chem. Phys.* **1985**, *82*, 736.
(178) Wanna, J.; Bernstein, E. R. *J. Chem. Phys.* **1986**, *84*, 927.
(179) Wanna, J.; Menapace, J. A.; Bernstein, E. R. *J. Chem. Phys.* **1986**, *85*, 1795.
(180) Menapace, J. A.; Bernstein, E. R. *J. Phys. Chem.* **1987**, *91*, 2533.
(181) Wanna, J.; Bernstein, E. R. *J. Chem. Phys.* **1987**, *86*, 6707.
(182) Menapace, J. A.; Bernstein, E. R. *J. Phys. Chem.* **1987**, *91*, 2843.
(183) Law, K. S.; Bernstein, E. R. *J. Chem. Phys.* **1985**, *82*, 2856;
(184) Nimlos, M. R.; Young, M. A.; Bernstein, E. R.; Kelley, D. F. *J. Chem. Phys.* **1989**, *91*, 5268.
(185) Li, S.; Bernstein, E. R. *J. Chem. Phys.* **1992**, *97*, 804.
(186) Fernandez, J. A.; Bernstein, E. R. *J. Chem. Phys.* **1997**, *106*, 3029.
(187) Disselkamp, R.; Bernstein, E. R. *J. Chem. Phys.* **1993**, *98*, 4339.
(188) Cheney, B. V.; Schulz, M.; Cheney, J.; Richards, W. G. *J. Am. Chem. Soc.* **1988**, *110*, 4195. Cheney, B. V.; Schulz, M. *J. Phys. Chem.* **1990**, *94*, 6268.
(189) Brédas, J. L.; Street, G. B. *J. Chem. Phys.* **1989**, *90*, 7291.
(190) Sapse, A. M.; Jain, D. C. *Chem. Phys. Lett.* **1986**, *124*, 517.
(191) Rodham, D. A.; Suzuki, S.; Suenram, R. D.; Lovas, F. J.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Nature* **1993**, *362*, 735.
(192) Sakaki, S.; Kato, K.; Miyazaki, T.; Musashi, Y.; Ohkubo, K.; Ihara, H.; Hirayama, C. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 659.
(193) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Phys. Chem. A* **1999**, *103*, 8265.
(194) Hobza, P.; Špirko, V.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem. A* **1998**, *102*, 2501.
(195) Hobza, P.; Špirko, V.; Havlas, Z.; Buchhold, K.; Reimann, B.; Barth, H.-D.; Brutschy, B. *Chem. Phys. Lett.* **1999**, *299*, 180.
(196) Hu, Y.; Yang, X.; Yang, S. *J. Chem. Phys.* **1999**, *111*, 134.
(197) Hermida-Ramón, H.; Peña-Gallego, A.; Martínez-Núñez, E.; Fernández-Ramos, A.; Cabaleiro-Lago, E. M. *J. Mol. Struct. (THEOCHEM)***2000**, *497*, 105.
(198) Špirko, V.; Engkvist, O.; Soldán, P.; Selzle, H. L.; Schlag, E. W.; Hobza, P. *J. Chem. Phys.* **1999**, *111*, 572.
(199) Engkvist, O.; Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Chem. Phys.* **1999**, *110*, 5758.
(200) Hirata, T.; Ikeda, H.; Saigusa, H. *J. Phys. Chem. A* **1999**, *103*, 1014.
(201) Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem.* **1996**, *100*, 18790.
(202) Jaffe, R. L.; Smith, G. D. *J. Chem. Phys.* **1996**, *105*, 2780.
(203) Krätzschmar, O.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem.* **1994** *98*, 3501.
(204) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Dougherty, D. A.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **1997**, *36*, 248.
(205) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641.
(206) Cozzi, F.; Ponzini, F.; Annunziata, R.; Cinquini, M.; Siegel, J. S. *Angew. Chem., Int. Ed.* **1995**, *34*, 1019.
(207) West, A. P., Jr.; Mecozzi, S.; Dougherty, D. A. *J. Phys. Org. Chem.* **1997**, *10*, 347.
(208) Williams, J. H.; Cockcroft, J. K.; Fitch, A. N. *Angew. Chem., Int. Ed.* **1992**, *31*, 1655.
(209) Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Chem. Phys.* **1990**, *93*, 5893.
(210) Columberg, G.; Bauder, A. *J. Chem. Phys.* **1997**, *106*, 504.
(211) Lukeš, V.; Breza, M.; Biskupič, S. *Theor. Chem. Acc.* **1999**, *101*, 319.

(212) Abdoul-Carime, H.; Wakisaka, A.; Flugge, J.; Takeo, H.; Periquet, V.; Schermann, J. P.; Desfrançois, C. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 4289.
(213) Sugawara, K.-I.; Miyawaki, J.; Nakanaga, T.; Takeo, H.; Lembach, G.; Djafari, S.; Barth, H.-D.; Brutschy, B. *J. Phys. Chem.* **1996**, *100*, 17145.
(214) Yeh, J.-H.; Shen, T.-L.; Nocera, D. G.; Leroi, G. E.; Suzuka, I.; Ozawa, H.; Namuta, Y. *J. Phys. Chem.* **1996**, *100*, 4385.
(215) Chipot, C.; Jaffe, R.; Maigret, B.; Pearlman, D. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 11217.
(216) Ishikawa, S.; Ebata, T.; Ishikawa, H.; Inoue, T.; Mikami, N. *J. Phys. Chem.* **1996**, *100*, 10531.
(217) Joireman, P. W.; Ohline, S. M.; Felker, P. M. *J. Phys. Chem. A* **1998**, *102*, 4481.
(218) Maxton, P. M.; Schaeffer, M. W.; Ohline, S. M.; Kim, W.; Venturo, V. A.; Felker, P. M. *J. Chem. Phys.* **1994**, *101*, 8391.
(219) Pryor, B. A.; Andrews, P. M.; Palmer, P. M.; Topp, M. R. *Chem. Phys. Lett.* **1997**, *267*, 531. Stratton, J. R.; Troxler, T.; Pryor, B. A.; Smith, P. G.; Topp, M. R. *J. Phys. Chem.* **1995**, *99*, 1424.
(220) Tsuzuki, S.; Uchimaru, T.; Matsumura, K.; Mikami, M.; Tanabe, K. *Chem. Phys. Lett.* **2000**, *319*, 547.
(221) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2000**, *122*, 3746.
(222) Gonzalez, C.; Lim, E. C. *J. Phys. Chem. A* **2000**, *104*, 2953.
(223) Ryjáček, F.; Kratchovíl, M.; Hobza, P. *Chem. Phys. Lett.* **1999**, *313*, 393.
(224) Gervasio, F. L.; Procacci, P.; Cardini, G.; Guarna, A.; Giolitti, A.; Schettino, V. *J. Phys. Chem. B* **2000**, *104*, 1108.
(225) Plokhotnichenko, A. M.; Radchenko, E. D.; Stepanian, S. G.; Adamowicz, L. *J. Phys. Chem. A* **1999**, *103*, 11052.
(226) Novoa, J. J.; Mota, F. *Chem. Phys. Lett.* **2000**, *318*, 345.
(227) Šponer, J.; Gabb, H. A.; Leszczynski, J.; Hobza, P. *Biophys. J.* **1997**, *73*, 76.
(228) Florián, J.; Šponer, J.; Warshel, A. *J. Phys. Chem. B* **1999**, *103*, 884.
(229) Hunter, C. A. *Chem. Soc. Rev.* **1994**, 101.
(230) Boyd. D. R.; Evans, T. A.; Jennings, B.; Malone, J. F.; O'Sullivan, W.; Smith, A. J. *Chem. Commun.* **1996**, 229.
(231) Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23.
(232) Brocchieri, L.; Karlin, S. *Proc. Natl. Acad. Sci. U.S.A.* **1994**, *91*, 9297.
(233) Mitchell, J. B. O.; Nandi, C. L.; McDonald, I. K.; Thornton, J. M.; Price, S. L. *J. Mol. Biol.* **1994**, *239*, 315.
(234) Alagona, G.; Ghio, C.; Monti, S. *J. Phys. Chem. A* **1998**, *102*, 6152.
(235) Dunitz, J. D.; Gavezzotti, A. *Acc. Chem. Res.* **1999**, *32*, 677.
(236) Cabaço, M. I.; Danten, Y.; Besnard, M.; Guissani, Y.; Guillot, B. *J. Phys. Chem. B* **1998**, *102*, 10712.
(237) Philip, D.; Robinson, J. M. A. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1643.
(238) Maier, G.; Lautz, Ch. *Eur. J. Org. Chem.* **1998**, *769*, 9.
(239) Resende, S. M.; De Almeida, W. B. *Chem. Phys.* **1996**, *206*, 1.
(240) Karpfen, A. *J. Phys. Chem. A* **1999**, *103*, 11431.
(241) Cardelino, B. H.; Moore, C. E.; Frazier, D. O.; Musaev, D. G.; Morokuma, K. *Int. J. Quantum Chem.* **1998**, *66*, 189.
(242) Karpfen, A. *J. Phys. Chem. A* **1998**, *102*, 9286.
(243) Karpfen, A. *J. Phys. Chem.* **1996**, *100*, 13474.
(244) Tsuzuki, S.; Uchimaru, T.; Tanabe, K. *Chem. Phys. Lett.* **1998**, *287*, 202.
(245) Tsuzuki, S.; Tanabe, K. *J. Phys. Chem.* **1992**, *96*, 10804.
(246) Wasiutynski, T.; van der Avoird, A.; Berns, R. M. *J. Comput. Chem.* **1978**, *69*, 5288.
(247) Glauser, W. A.; Raber, D. J.; Stevens, B. *J. Comput. Chem.* **1988**, *9*, 539.
(248) Malar, E. J. P.; Chandra, A. K. *J. Phys. Chem.* **1981**, *85*, 2190.
(249) Alberts, I. L.; Rowlands, T. W.; Handy, N. C. *J. Chem. Phys.* **1988**, *88*, 3811.
(250) Chan, M. C.; Block, P. A.; Miller, R. E. *J. Chem. Phys.* **1995**, *102*, 3993.
(251) van Nes, G. J. H.; Vos, A. *Acta Crystallogr. B* **1977**, *33*, 1653.
(252) Rytter, E.; Gruen, D. M. *Spectrochim. Acta A* **1979**, *35*, 199.
(253) Battaglia, M. R.; Buckingham, A. D.; Williams, J. H. *Chem. Phys. Lett.* **1981**, *78*, 421.
(254) Vrbancich, J.; Ritchie, G. L. D. *Chem. Phys. Lett.* **1983**, *94*, 63.
(255) Williams, J. H. *Acc. Chem. Res.* **1993**, *26*, 593.
(256) Amos, A. T.; Cohen, S. M.; Kettley, J. C.; Palmer, T. F.; Simons, J. P. In *Structure and Dynamics of Weakly Bound Complexes*; Weber, A., Ed.; Reidel: Dordrecht, 1987; p 263.
(257) Stone, A. J.; Tsuzuki, S. *J. Phys. Chem. B* **1997**, *101*, 10178.
(258) Grabowski, S. J. *Pol. J. Chem.* **1995**, *69*, 223.
(259) Heaton, N. J.; Bello, P.; Herradón, B.; del Campo, A.; Jiménez-Barbero, J. *J. Am. Chem. Soc.* **1998**, *120*, 9632.
(260) Heaton, N. J.; Bello, P.; Herradón, B.; del Campo, A.; Jiménez-Barbero, J. *J. Am. Chem. Soc.* **1998**, *120*, 12371.
(261) Kim, D. H.; Lee, S. S.; Whang, D.; Kim, K. *Bioorg. Med. Chem. Lett.* **1993**, *3*, 263. Ren, T.; Jin, Y.; Kim, K. S.; Kim, D. H. *J. Biomol. Struct. Dyn.* **1997**, *15*, 401. Hong, B. H.; Lee, J. Y.; Cho, S. J.; Yun, S.; Kim, K. S. *J. Org. Chem.* **1999**, *64*, 5661.
(262) Schladetzky, K. D.; Haque, T. S.; Gellman, S. H. *J. Org. Chem.* **1995**, *60*, 4108.
(263) Newcomb, L. F.; Haque, T. S.; Gellman, S. H. *J. Am. Chem. Soc.* **1995**, *117*, 6509.
(264) Shetty, A. S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019.
(265) Paliwal, S.; Geib, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 4497.
(266) Adams, H.; Carver, F. J.; Hunter, C. A.; Morales, J. C.; Seward, E. M. *Angew. Chem., Int. Ed.* **1996**, *35*, 1542.
(267) Dougherty, D. A.; Stauffer, D. *Science* **1990**, *250*, 1558.
(268) Kumpf R. A.; Dougherty, D. A. *Science* **1993**, *261*, 1708.
(269) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.
(270) Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 4177.
(271) Pullman, A.; Berthier, G.; Savinelli, R. *J. Comput. Chem.* **1997**, *18*, 2012. Pullman, A.; Berthier, G.; Savinelli, R. *J. Am. Chem. Soc.* **1998**, *120*, 8553.
(272) Donini, O.; Weaver, D. F. *J. Comput. Chem.* **1998**, *19*, 1515.
(273) Luque, E. J.; Orozco, M. *J. Comput. Chem.* **1998**, *19*, 866.
(274) Nicholas, J. B.; Hay, B. P.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103*, 1394.
(275) Nicholas, J. B.; Hay, B. P. *J. Phys. Chem. A* **1999**, *103*, 9815.
(276) Cubero, E.; Orozco, M.; Luque, F. J. *J. Phys. Chem. A* **1999**, *103*, 315.
(277) Zhu, W.; Jiang, H.; Puah, C. M.; Tan, X.; Chen, K.; Cao, Y.; Ji, R. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2615.
(278) Minoux, H.; Chipot, C. *J. Am. Chem. Soc.* **1999**, *121*, 10366.
(279) Gallivan, J. P.; Dougherty, D. A. *J. Am. Chem. Soc.* **2000**, *122*, 870.
(280) Norrby, P.-O.; Liljefors, T. *J. Am. Chem. Soc.* **1999**, *121*, 2303.
(281) Bartoli, S.; Roelens, S. *J. Am. Chem. Soc.* **1999**, *121*, 11908.
(282) Berg, C.; Beyer, M.; Achatz, U.; Joos, S.; Niedner-Schatteburg, G.; Bondybey, V. E. J. *J. Chem. Phys.* **1998**, *108*, 5398.
(283) Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501.
(284) Guo, B. C.; Purnell, J. W.; Castleman, A. W. *Chem. Phys. Lett.* **1990**, *168*, 155.
(285) Sunner, J.; Nishizawa, K.; Kebarle, P. *J. Phys. Chem.* **1981**, *85*, 1814.
(286) Cubero, E.; Luque, F. J.; Orozco, M. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 5876.
(287) Ryzhov, V.; Dunbar, R. C. *J. Am. Chem. Soc.* **1999**, *121*, 2259.
(288) Dunbar, R. C. *J. Phys. Chem. A* **1998**, *102*, 8946.
(289) Mecozzi, S.; West, A. P., Jr.; Dougherty, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 10566.
(290) De Wall, S. L.; Meadows, E. S.; Barbour, L. J.; Gokel, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 5613.
(291) Miklis, P. C.; Ditchfield, R.; Spencer, T. A. *J. Am. Chem. Soc.* **1998**, *120*, 10482.
(292) Raos, G.; Astorri, L.; Raimondi, M.; Cooper, D. L.; Gerratt, J.; Karadakov, P. B. *J. Phys. Chem. A* **1997**, *101*, 2886.
(293) Schleyer, P. v. R.; Buzek, P.; Muller, T.; Apeloig, Y.; Siehl, H.-U. *Angew. Chem., Int. Ed.* **1993**, *32*, 1471.
(294) Olsson, L.; Cremer, D. *Chem. Phys. Lett.* **1993**, *215*, 433.
(295) Ottosson, C.-H.; Cremer, D. *Organometallics* **1996**, *15*, 5495.
(296) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Phys. Chem.* **1985**, *89*, 5222.
(297) Kim, K. S.; Lee, J. Y.; Lee, S. J.; Ha, T.-K.; Kim, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 7399.
(298) Lee, J. Y.; Lee, S. J.; Choi, H. S.; Cho, S. J.; Kim, K. S.; Ha, T.-K. *Chem. Phys. Lett.* **1995**, *232*, 67.
(299) Berthomieu, D.; Brenner, V.; Ohanessian, G.; Denhez, J. P.; Millié, P.; Audier, H. E. *J. Phys. Chem.* **1995**, *99*, 712.
(300) Dyke, T. R.; Muenter, J. S. *J. Chem. Phys.* **1972**, *57*, 5011. Dyke, T. R.; Muenter, J. S. *J. Chem. Phys.* **1974**, *60*, 2929. Dyke, T. R.; Mack, K. M.; Muenter, J. S. *J. Chem. Phys.* **1977**, *66*, 498. Odutola, J. A.; Dyke, T. R. *J. Chem. Phys.* **1980**, *72*, 5062.
(301) Curtiss, L. A.; Frurip, D. L.; Blander, M. *J. Chem. Phys.* **1979**, *71*, 2703.
(302) Liu, K.; Loeser, J. G.; Elrod, M. J.; Host, B. C.; Rzepiela, J. A.; Saykally, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 3507. Liu, K.; Cruzan, J. D.; Saykally, R. J. *Science* **1996**, *271*, 929. Liu, K.; Brown, M. G.; Carter, C.; Saykally, R. J.; Gregory, J. K.; Clary, D. C. *Nature* **1996**, *381*, 501. Cruzan, J. D.; Braly, L. B.; Liu, K.; Brown, M. G.; Loeser, J. G.; Saykally, R. J. *Science* **1996**, *271*, 59. Cruzan, J. D.; Brown, M. G.; Liu, K.; Braly, L. B.; Saykally, R. J. *J. Chem. Phys.* **1996**, *105*, 6634. Liu, K.; Brown, M. G.; Cruzan, J. D.; Saykally, R. J. *J. Phys. Chem. A* **1997**, *101*, 9011. Liu, K.; Brown, M. G.; Saykally, R. J. *J. Phys. Chem. A* **1997**, *101*, 8995. Cruzan, J. D.; Viant, M. R.; Brown, M. G.; Saykally, R. J. *J. Phys. Chem. A* **1997**, *101*, 9022. Brown, M. G.; Keutsch, F. N.; Saykally, R. J. *J. Chem. Phys.* **1998**, *109*, 9645. Viant, M. R.; Brown, M. G.; Cruzan, J. D.; Saykally, R. J.; Geleijns, M.; van der Avoird, A. *J. Chem. Phys.* **1999**, *110*, 4369. Fellers, R. S.; Braly, L. B.; Saykally, R. J.; Leforestier, C. *J. Chem. Phys.* **1999**, *110*, 6306. Paul, J. B.; Provencal, R. A.; Chapo, C.; Roth, K.; Casaes, R.; Saykally, R. J. *J. Phys. Chem. A* **1999**, *103*, 2972. Brown, M. G.; Viant, M. R.; McLaughlin, R.

P.; Keoshian, C. J.; Michael, E.; Cruzan, J. D.; Saykally, R. J.; van der Avoird, A. *J. Chem. Phys.* **1999**, *111*, 7789. Brown, M. G.; Keutsch, F. N.; Braly, L. B.; Saykally, R. J. *J. Chem. Phys.* **1999**, *111*, 7801.
(303) Fellers, R. S.; Leforestier, C.; Braly, L. B.; Brown, M. G.; Saykally, R. J. *Science* **1999**, *284*, 945.
(304) Huisken, F.; Kaloudis, M.; Kulcke, A. *J. Chem. Phys.* **1996**, *104*, 17.
(305) Brudermann, J.; Lohbrandt, P.; Buck, U.; Buch, V. *Phys. Rev. Lett.* **1998**, *80*, 2821. Brudermann, J.; Melzer, M.; Buck, U.; Kazimirski, J. K.; Sadlej, J.; Buch, V. *J. Chem. Phys.* **1999**, *110*, 10649.
(306) Buck, U.; Ettischer, I.; Melzer, M.; Buch, V.; Sadlej, J. *Phys. Rev. Lett.* **1998**, *80*, 2578.
(307) Devlin, J. P.; Joyce, C.; Buch, V. *J. Phys. Chem. A* **2000**, *104*, 1974.
(308) Scheiner, S. *Annu. Rev. Phys. Chem.* **1994**, *45*, 23.
(309) Kim, K. S.; Dupuis, M.; Lie, G. C.; Clementi, E. *Chem. Phys. Lett.* **1986**, *131*, 451.
(310) Mhin, B. J.; Kim, H. S.; Kim, H. S.; Yoon, C. W.; Kim, K. S. *Chem. Phys. Lett.* **1991**, *176*, 41. Mhin, B. J.; Lee, S. J.; Kim, K. S. *Phys. Rev. A.* **1993**, *48*, 3764. Mhin, B. J.; Kim, J.; Lee, S.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **1994**, *100*, 4484. Kim, J.; Mhin, B. J.; Lee, S. J.; Kim, K. S. *Chem. Phys. Lett.* **1994**, *219*, 243. Kim, J.; Lee, J. Y.; Lee, S.; Mhin, B. J.; Kim, K. S. *J. Chem. Phys.* **1995**, *102*, 310. Kim, J.; Majumdar, D.; Lee, H. M.; Kim, K. S. *J. Chem. Phys.* **1999**, *110*, 9128. Lee, H. M.; Suh, S. B.; Lee, J. Y.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 9759.
(311) Kim, K.; Jordan, K. D. *J. Phys. Chem.* **1994**, *98*, 10089. Tsai, C. J.; Jordan, K. D. *Chem. Phys. Lett.* **1993**, *213*, 181. Pedulla, J. M.; Vila, F.; Jordan, K. D. *J. Chem. Phys.* **1996**, *105*, 11091. Pedulla, J. M.; Kim, K.; Jordan, K. D. *Chem. Phys. Lett.* **1998**, *291*, 78.
(312) Kim, K.; Jordan, K. D.; Zwier, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 11568.
(313) Gregory, J. K.; Clary, D. C. *J. Phys. Chem.* **1996**, *100*, 18014. Gregory, J. K.; Clary, D. C. *J. Chem. Phys.* **1995**, *103*, 8924.
(314) Wales, D. J.; Walsh, T. R. *J. Chem. Phys.* **1997**, *106*, 7193. Wales, D. J.; Walsh, T. R. *J. Chem. Phys.* **1996**, *105*, 6957.
(315) Feyereisen, M. W.; Feller, D.; Dixon, D. A. *J. Phys. Chem.* **1996**, *100*, 2993.
(316) Leforestier, C.; Braly, L. B.; Liu, K.; Elrod, M. J.; Saykally, R. J. *J. Chem. Phys.* **1997**, *106*, 8527. Fellers, R. S.; Braly, L. B.; Saykally, R. J.; Leforestier, C. *J. Chem. Phys.* **1999**, *110*, 6306.
(317) Millot, C.; Soetens, J.-C.; Martins Costa, M. T. C.; Hodges, M. P.; Stone, A. J. *J. Phys. Chem. A* **1998**, *102*, 754. Hodges, M. P.; Stone, A. J.; Xantheas, S. *J. Phys. Chem. A* **1997**, *101*, 9163.
(318) Chen, H.; Liu, S.; Light, J. C. *J. Chem. Phys.* **1999**, *110*, 168. Lee, C.; Chen, H.; Fitzgerald, G. *J. Chem. Phys.* **1995**, *102*, 1266.
(319) Hartke, B.; Schütz, M.; Werner, H.-J. *Chem. Phys.* **1998**, *239*, 561. Schütz, M.; Rauhut, G.; Werner, H.-J. *J. Phys. Chem. A* **1998**, *102*, 5997.
(320) Xantheas, S. S.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 8774.
(321) Xantheas, S. S. *J. Chem. Phys.* **1994**, *100*, 7523.
(322) Xantheas, S. S.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 8037. Xantheas, S. S. *J. Chem. Phys.* **1995**, *102*, 4505.
(323) Bürgi, T.; Graf, S.; Leutwyler, S.; Klopper, W. *J. Chem. Phys.* **1995**, *103*, 1077. Sabo, D.; Bačić, Z.; Bürgi, T.; Leutwyler, S. *Chem. Phys. Lett.* **1995**, *244*, 283. Sabo, D.; Bačić, Z.; Graf, S.; Leutwyler, S. *Chem. Phys. Lett.* **1996**, *261*, 318. Klopper, W.; Schütz, M.; Lüthi, H. P.; Leutwyler, S. *J. Chem. Phys.* **1995**, *103*, 1085. Klopper, W.; Scütz, M. *Chem. Phys. Lett.* **1995**, *237*, 536. Schütz, M.; Klopper, W.; Lüthi, H.-P.; Leutwyler, S. *J. Chem. Phys.* **1995**, *103*, 6114. Graf, S.; Mohr, W.; Leutwyler, S. *J. Chem. Phys.* **1999**, *110*, 7893.
(324) van der Avoird, A.; Olthof, E. H. T.; Wormer, P. E. S. *J. Chem. Phys.* **1996**, *105*, 8034. Olthof, E. H. T.; van der Avoird, A.; Wormer, P. E. S.; Liu, K.; Saykally, R. J. *J. Chem. Phys.* **1996**, *105*, 8051. Geleijns, M.; van der Avoird, A. *J. Chem. Phys.* **1999**, *110*, 823.
(325) van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *Chem. Phys. Lett.* **1995**, *237*, 560.
(326) Estrin, D. A.; Paglieri, L.; Corongiu, G.; Clementi, E. *J. Phys. Chem.* **1996**, *100*, 8701.
(327) Kloppper, W.; Lüthi, H. P. *Mol. Phys.* **1999**, *96*, 559.
(328) Gresh, N. *J. Phys. Chem. A* **1997**, *101*, 8680.
(329) Masella, M.; Gresh, N.; Flament, J.-P. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2745.
(330) Fowler, J. E.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 446.
(331) Guiang, C. S.; Wyatt, R. E. *Int. J. Quantum Chem.* **1998**, *68*, 233.
(332) Loerting, T.; Liedl, K. R.; Rode, B. M. *J. Chem. Phys.* **1998**, *109*, 2672.
(333) Koehler, J. E. H.; Saenger, W.; Lesyng, B. *J. Comput. Chem.* **1987**, *8*, 1090.
(334) Lee, C.; Chen, H.; Fitzgerald, G. *J. Chem. Phys.* **1994**, *101*, 4472.
(335) Sremaniak, L. S.; Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1996**, *105*, 3715.
(336) Sadlej, J.; Buch, V.; Kazimirski, J. K.; Buck, U. *J. Phys. Chem. A* **1999**, *103*, 4933.
(337) Specchio, R.; Famulari, A.; Sironi, M.; Raimondi, M. *J. Chem. Phys.* **1999**, *111*, 6204.
(338) Odutola, J. A.; Viswanathan, R.; Dyke, T. R. *J. Am. Chem. Soc.* **1979**, *101*, 4787.
(339) Kay, B. D.; Castleman, A. W. *J. Phys. Chem.* **1985**, *89*, 4867.
(340) Buck, U.; Gu, X.; Lauenstein, C.; Rudolph, A. *J. Phys. Chem.* **1988**, *92*, 5561. Buck, U.; Schmidt, B.; Siebers, J.-G. *J. Chem. Phys.* **1993**, *99*, 9428. Buck, U.; Ettischer, I. *J. Chem. Phys.* **1994**, *100*, 6974. Buck, U.; Ettischer, I. *Faraday Discuss.* **1994**, *97*, 215. Buck, U. *J. Phys. Chem.* **1994**, *98*, 5190. Buck, U.; Siebers, J. G.; Wheatley, R. J. *J. Chem. Phys.* **1998**, *108*, 20;
(341) Buck, U.; Ettischer, I. *J. Chem. Phys.* **1998**, *108*, 33.
(342) Swanton, D. J.; Backsay, G. B.; Hush, N. S. *Chem. Phys.* **1983**, *82*, 303.
(343) Weltner, W.; Pitzer, K. S. *J. Am. Chem. Soc.* **1951**, *73*, 2606.
(344) Lovas, F. J.; Belov, S. P.; Tretyakov, M. Y.; Stahl, W.; Suenram, R. D. *J. Mol. Spectrosc.* **1995**, *170*, 478. Lovas, F. J.; Hartwig, H. *J. Mol. Spectrosc.* **1997**, *185*, 98. Lugez, C. L.; Lovas, F. J.; Hougen, J. T.; Ohashi, N. *J. Mol. Spectrosc.* **1999**, *194*, 95.
(345) Huisken, F.; Kaloudis, M.; Koch, M.; Werhahn, O. *J. Chem. Phys.* **1996**, *105*, 8965.
(346) Provencal, R. A.; Paul, J. B.; Roth, K.; Chapo, C.; Casaes, R. N.; Saykally, R. J.; Tschumper, G. S.; Schaefer, H. F., III *J. Chem. Phys.* **1999**, *110*, 4258.
(347) Mó, O.; Yáñez, M.; Elguero, J. *J. Mol. Struct. (THEOCHEM)* **1994**, *314*, 73.
(348) Bleiber, A.; Sauer, J. *Chem. Phys. Lett.* **1995**, *238*, 243.
(349) Williams, R. W.; Cheh, J. L.; Lowrey, A. H.; Weir, A. F. *J. Phys. Chem.* **1995**, *99*, 5299.
(350) Mó, O.; Yáñez, M.; Elguero, J. *J. Chem. Phys.* **1997**, *107*, 3592.
(351) Hagernmeister, F. C.; Gruenloh, C. J.; Zwier, T. S. *J. Phys. Chem. A* **1998**, *102*, 82.
(352) Tschumper, G. S.; Gonzales, J. M.; Schaefer, H. F., III *J. Chem. Phys.* **1999**, *111*, 3027.
(353) Huisken, F.; Stemmler, M. *Chem. Phys. Lett.* **1991**, *180*, 332.
(354) Bakkas, N.; Bouteiller, Y.; Loutellier, A.; Perchard, J. P.; Racine, S. *J. Chem. Phys.* **1993**, *99*, 3335.
(355) Bakkas, N.; Bouteiller, Y.; Loutellier, A.; Perchard, J. P.; Racine, S. *Chem. Phys. Lett.* **1995**, *232*, 90.
(356) Stockman, P. A.; Blake, G. A.; Lovas, F. J.; Suenram, R. D. *J. Chem. Phys.* **1997**, *107*, 3782.
(357) Huisken, F.; Pooran, S. M.; Werhahn, O. *Chem. Phys.* **1998**, *49*, 11.
(358) Markham, G. D.; Glusker, J. P.; Bock, C. L.; Trachtman, M.; Bock, C. W. *J. Phys. Chem.* **1996**, *100*, 3488.
(359) Glendening, E. D.; Feller, D. *J. Phys. Chem.* **1996**, *100*, 4790. Feller, D.; Glendening, E. D.; Kendall, R. A.; Peterson, K. A. *J. Chem. Phys.* **1994**, *100*, 4981. Glendening, E. D.; Feller, D. *J. Phys. Chem.* **1995**, *99*, 3060. Feller, D.; Glendening, E. D.; Woon, D. E.; Feyereisen, M. W. *J. Chem. Phys.* **1995**, *103*, 3526. Feller, D. *J. Phys. Chem. A* **1997**, *101*, 2723.
(360) Bagno, A.; Conte, V.; Furia, F. D.; Moro, S. *J. Phys. Chem. A* **1997**, *101*, 4637.
(361) Marcos, E. S.; Martínez, J. M.; Pappalardo, R. R. *J. Chem. Phys.* **1996**, *105*, 5968. Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1996**, *105*, 2938.
(362) Islam, M. S.; Pethrick, R. A.; Pugh, D. *J. Phys. Chem. A* **1998**, *102*, 2201.
(363) Mhin, B. J.; Lee, S.; Cho, S. J.; Lee, K.; Kim, K. S. *Chem. Phys. Lett.* **1992**, *197*, 77. Mhin, B. J.; Kim, J.; Kim, K. S. *Chem. Phys. Lett.* **1993**, *216*, 305. Lee, S.; Kim, J.; Park, J. K.; Kim, K. S. *J. Phys. Chem.* **1996**, *100*, 14329. Lee, H. M.; Kim, J.; Lee, S.; Mhin, B. J.; Kim, K. S. *J. Chem. Phys.* **1999**, *111*, 3995.
(364) Smith, D. M. A.; Smets, J.; Elkadi, Y.; Adamowicz, L. *J. Chem. Phys.* **1997**, *107*, 5788. Smith, D. M. A.; Smets, J.; Elkadi, Y.; Adamowicz, L. *J. Chem. Phys.* **1998**, *109*, 1238. Smith, D. M. A.; Smets, J.; Adamowicz, L. *J. Chem. Phys.* **1999**, *110*, 3804.
(365) Skurski, P.; Gutowski, M. *J. Chem. Phys.* **1998**, *108*, 6303.
(366) Tsurusawa, T.; Iwata, S. *Chem. Phys. Lett.* **1998**, *287*, 553.
(367) Tachikawa, H.; Ogasawara, M. *J. Phys. Chem.* **1990**, *94*, 1746. Clark, T.; Illing, G. *J. Am. Chem. Soc.* **1987**, *109*, 1013.
(368) Kim, K. S.; Park, I.; Lee, S.; Cho, K.; Lee, J. Y.; Kim, J.; Joannopoulos, J. D. *Phys. Rev. Lett.* **1996**, *76*, 956. Lee, S.; Lee, S. J.; Lee, J. Y.; Kim, J.; Kim, K. S.; Park, I.; Cho, K.; Joannopoulos, J. D. *Chem. Phys. Lett.* **1996**, *254*, 128. Kim, J.; Park, J. M.; Oh, K. S.; Lee, J. Y.; Lee, S.; Kim, K. S. *J. Chem. Phys.* **1997**, *106*, 10207. Kim, K. S.; Lee, S.; Kim, J.; Lee, J. Y. *J. Am. Chem. Soc.* **1997**, *119*, 9329. Lee, S.; Kim, J.; Lee, S. J.; Kim, K. S. *Phys. Rev. Lett.* **1997**, *79*, 2038. Kim, J.; Lee, J. Y.; Oh, K. S.; Park, J. M.; Lee, S.; Kim, K. S. *Phys. Rev. A* **1999**, *59*, R930. Kim, J.; Suh, S. B.; Kim, K. S. *J. Chem. Phys.* **1999**, *111*, 10077. Baik, J.; Kim, J.; Majumdar, D.; Kim, K. S. *J. Chem. Phys.* **1999**, *110*, 9116. Majumdar, D.; Kim, J.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 101. Lee, H. M.; Suh, S. B.; Kim, K. S. *Bull. Kor. Chem. Soc.* **2000**, *21*, 555. Suh, S. B.; Lee, H. M.; Kim,

J.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **2000**, in press. Kim, J.; Lee, H. M.; Suh, S. B.; Majumdar, D.; Kim, K. S. *J. Chem. Phys.* **2000**, in press.
(369) Del Bene, J. E. *Chem. Phys. Lett.* **1974**, *24*, 203.
(370) Frisch, M. J.; Pople, J. A.; Del Bene, J. E. *J. Chem. Phys.* **1983**, *78*, 4063.
(371) Engdahl, A.; Nelander, B. *Chem. Phys. Lett.* **1983**, *100*, 129.
(372) Engdahl, A.; Nelander, B. *Chem. Phys. Lett.* **1985**, *113*, 49.
(373) Peterson, K. I.; Klemperer, W. *J. Chem. Phys.* **1986**, *85*, 725.
(374) Andrews, A. M.; Kuczkowski, R. L. *J. Chem. Phys.* **1993**, *98*, 791.
(375) Engdahl, A.; Nelander, B. *J. Phys. Chem.* **1985**, *89*, 2860.
(376) Engdahl, A.; Nelander, B. *J. Phys. Chem.* **1987**, *91*, 2253.
(377) Bornsen, K. O.; Selzle, H. L.; Schlag, E. W. *Z. Naturforsch. Teil A* **1990**, *45*, 1217.
(378) Gotch, A. J.; Garrett, A. W.; Severance, D. L.; Zwier, T. S. *Chem. Phys. Lett.* **1991**, *178*, 121.
(379) Gotch, A. J.; Zwier, T. S. *J. Chem. Phys.* **1992**, *96*, 3388.
(380) Garret, A. W.; Zwier, T. S. *J. Chem. Phys.* **1992**, *96*, 3402.
(381) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A.; Blake, G. A. *Science* **1992**, *257*, 942.
(382) Gutowsky, H. S.; Emilsson, T.; Arunan, E. *J. Chem. Phys.* **1993**, *99*, 4883.
(383) Pribble, R. N.; Zwier, T. S. *Science* **1994**, *265*, 75.
(384) Pribble, R. N.; Zwier, T. S. *Faraday Discuss.* **1994**, *97*, 229.
(385) Cheng, B.-M.; Grover, J. R.; Walters, E. A. *Chem. Phys. Lett.* **1995**, *232*, 364.
(386) Pribble, R. N.; Garrett, A. W.; Haber, K.; Zwier, T. S. *J. Chem. Phys.* **1995**, *103*, 531.
(387) Maxton, P. M.; Schaeffer, M. W.; Felker, P. M. *Chem. Phys. Lett.* **1995**, *241*, 603.
(388) Gruenloh, C. J.; Carney, J. R.; Arrington, C. A.; Zwier, T. S.; Fredericks, S. Y.; Jordan, K. *Science* **1997**, *276*, 1678.
(389) Courty, A.; Mons, M.; Dimicoli, I.; Piuzzi, F.; Gaigeot, M.-P.; Brenner, V.; de Pujo, P.; Millié, P. *J. Phys. Chem. A* **1998**, *102*, 6590.
(390) Gruenloh, C. J.; Carney, J. R.; Hagemeister, F. C.; Arrington, C. A.; Zwier, T. S.; Fredericks, S. Y.; Wood, J. T.; Jordan, K. *J. Chem. Phys.* **1998**, *109*, 6601.
(391) Gruenloh, C. J.; Carney, J. R.; Hagemeister, F. C.; Zwier, T. S.; Wood, J. T., III; Jordan, K. D. *J. Chem. Phys.* **2000**, *113*, 2290.
(392) Emilsson, T.; Gutowsky, H. S.; de Oliveira, G.; Dykstra, C. E. *J. Chem. Phys.* **2000**, *112*, 1287.
(393) Linse, P.; Karlström, G.; Jönsson, B. *J. Am. Chem. Soc.* **1984**, *106*, 4096.
(394) Linse, P. *J. Comput. Chem.* **1988**, *9*, 505.
(395) Linse, P. *J. Am. Chem. Soc.* **1990**, *112*, 1744.
(396) Augspurger, J. D.; Dykstra, C. E.; Zwier, T. S. *J. Phys. Chem.* **1993**, *97*, 980.
(397) Fredericks, S. Y.; Jordan, K. D.; Zwier, T. S. *J. Phys. Chem.* **1996**, *100*, 7810.
(398) Gregory, J. K.; Clary, D. C. *Mol. Phys.* **1996**, *88*, 33.
(399) Sorenson, J. M.; Gregory, J. K.; Clary, D. C. *J. Chem. Phys.* **1997**, *106*, 849.
(400) Kim, K. S.; Lee, J. Y.; Choi, H. S.; Kim, J.; Jang, J. H. *Chem. Phys. Lett.* **1997**, *265*, 497.
(401) Fredericks, S. Y.; Pedulla, J. M.; Jordan, K. D.; Zwier, T. S. *Theor. Chem. Acc.* **1997**, *96*, 51.
(402) Benoit, D. M.; Chavagnac, A. X.; Clary, D. C. *Chem. Phys. Lett.* **1998**, *283*, 269.
(403) Tachikawa, H.; Igarashi, M. *J. Phys. Chem. A* **1998**, *102*, 8648.
(404) Kim, W.; Neuhauser, D.; Wall, M. R.; Felker, P. M. *J. Chem. Phys.* **1999**, *110*, 8461.
(405) Tarakeshwar, P.; Choi, H. S.; Lee, S. J.; Lee, J. Y.; Kim, K. S.; Ha, T.-K, Jang, J. H.; Lee, J. G.; Lee, H. *J. Chem. Phys.* **1999**, *111*, 5838.
(406) Dang, L. X.; Feller, D. *J. Phys. Chem. B* **2000**, *104*, 4403.
(407) Riehn, Ch.; Lahmann, Ch.; Wassermann, B.; Brutschy, B. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1161.
(408) Djafari, S.; Lembach, G.; Barth, H.-D.; Brutschy, B. *Z. Phys. Chem.* **1996**, *195*, 253.
(409) Barth, H.-D.; Buchhold, K.; Djafari, S.; Reimann, B.; Lommatzsch, U.; Brutschy, B. *Chem. Phys.* **1998**, *239*, 49.
(410) Brenner, V.; Martrenchanrd-Barra, S.; Millie, B.; Dedonder-Lardeux, C.; Jouvet, C.; Solgadi, D. *J. Phys. Chem.* **1995**, *99*, 5848.
(411) Danten, Y.; Tassaing, T.; Besnard, M. *J. Phys. Chem. A* **1999**, *103*, 3530.
(412) Gallivan, J. P.; Dougherty, D. A. *Org. Lett.* **1999**, *1*, 103.
(413) Tarakeshwar, P.; Kim, K. S.; Brutschy, B. *J. Chem. Phys.* **1999**, *110*, 8501.
(414) Tarakeshwar, P.; Kim, K. S.; Brutschy, B. *J. Chem. Phys.* **2000**, *112*, 1769.
(415) Li, S.; Bernstein, E. R. *J. Chem. Phys.* **1992**, *97*, 792.
(416) Palmer, P. M.; Topp, M. R. *Chem. Phys.* **1998**, *239*, 65.
(417) Spoerel, U.; Stahl, W. *J. Mol. Spectrosc.* **1998**, *190*, 278.
(418) Samanta, U.; Chakrabarti, P.; Chandrasekhar, J. *J. Phys. Chem. A* **1998**, *102*, 8964.
(419) Short, K. W.; Callis, P. R. *J. Chem. Phys.* **1998**, *108*, 10189.
(420) Korter, T. M.; Pratt, D. W.; Küpper, J. *J. Phys. Chem. A* **1998**, *102*, 7211.
(421) Carney, J. R.; Hagemeister, F. C.; Zwier, T. S. *J. Chem. Phys.* **1998**, *108*, 3379.
(422) Helm, R. M.; Clara, M.; Grebner, Th. L.; Neusser, H. J. *J. Phys. Chem. A* **1998**, *102*, 3268.
(423) Huang, Y.; Sulkes, M. *J. Phys. Chem.* **1996**, *100*, 16479.
(424) Muino, P. L.; Callis, P. R. *Chem. Phys. Lett.* **1994**, *222*, 156.
(425) Arnold, S.; Sulkes, M. *J. Phys. Chem.* **1992**, *96*, 4768.
(426) Tubergen, M. J.; Levy, D. H. *J. Phys. Chem.* **1991**, *95*, 2175.
(427) Hager, J.; Ivanco, M.; Smith, M. A.; Wallace, S. C. *Chem. Phys. Lett.* **1985**, *113*, 503.
(428) Hager, J.; Wallace, S. C. *J. Phys. Chem.* **1984**, *88*, 5513.
(429) Carney, J. R.; Zwier, T. S. *J. Phys. Chem. A* **1999**, *103*, 9943.
(430) Mons, M.; Dimicoli, I.; Tardivel, B.; Piuzzi, F.; Brenner, V.; Millié, P. *J. Phys. Chem. A* **1999**, *103*, 9958.
(431) Carles, S.; Desfrançois, C.; Schermann, J. P.; Smith, D. M. A.; Adamowicz, L. *J. Chem. Phys.* **2000**, *112*, 3726.
(432) Pápai, I.; Jancsó, G. *J. Phys. Chem. A* **2000**, *104*, 2132.
(433) Lee, J. Y.; Kim, J.; Lee, H. M.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2000**, in press.
(434) Brutschy, B.; Eggert, J.; Janes, C.; Baumgärtel, H. *J. Phys. Chem.* **1991**, *95*, 5041.
(435) Fujii, A.; Okuyama, S.; Iwasaki, A.; Maeyama, T.; Ebata, T.; Mikami, N. *Chem. Phys. Lett.* **1996**, *256*, 1.
(436) Djafari, S.; Barth, H.-D.; Bucchold, K.; Brutschy, B. *J. Chem. Phys.* **1997**, *107*, 10573.
(437) Garrett, A. W.; Severance, D. L.; Zwier, T. S. *J. Chem. Phys.* **1992**, *96*, 7245.
(438) Garrett, A. W.; Zwier, T. S. *J. Chem. Phys.* **1992**, *96*, 7259.
(439) Pribble, R. N.; Hagemeister, F. C.; Zwier, T. S. *J. Chem. Phys.* **1997**, *106*, 2145.
(440) Hagemeister, F. C.; Gruenloh, C. J.; Zwier, T. S. *Chem. Phys.* **1998**, *239*, 83.
(441) Gruenloh, C. J.; Florio, G. M.; Carney, J. R.; Hagemeister, F. C.; Zwier, T. S. *J. Phys. Chem. A* **1999**, *103*, 496.
(442) Gruenloh, C. J.; Hagemeister, F. C.; Carney, J. R.; Zwier, T. S. *J. Phys. Chem. A* **1999**, *103*, 503.
(443) Buchhold, K.; Reimann, B.; Djafari, S.; Barth, H.-D.; Brutschy, B.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 1844.
(444) Riehn, C.; Buchhold, K.; Reimann, B.; Djafari, S.; Barth, H.-D.; Brutschy, B.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 1170.
(445) Michael, D.; Benjamin, I. *J. Phys. Chem.* **1995**, *99*, 1530.
(446) Ahmed, M.; Apps, C. J.; Hughes, C.; Watt, N. E.; Whitehead, J. C. *J. Phys. Chem. A* **1997**, *101*, 1250.
(447) Ikeguchi, M.; Shimizu, S.; Nakamura, S.; Shimizu, K. *J. Phys. Chem. B* **1998**, *102*, 5891.
(448) Unpublished results.
(449) Curren, D. J.; Springfield, J. L.; Knight, A. E. W. *Abstracts of Papers*; 8th Asian Chemical Congress, Nov 21, 1999; 1999, Vol. 8, p 285.
(450) Elrod, M. J.; Saykally, R. J. *Chem. Rev.* **1994**, *94*, 1975.
(451) Silva, S. C.; Devlin, J. P. *J. Phys. Chem.* **1994**, *98*, 10847.
(452) Caminati, W.; Melandri, S.; Rossi, I.; Favero, P. G. *J. Am. Chem. Soc.* **1999**, *121*, 10098.
(453) Ruiz, E.; Salahub, D. R.; Vela, A. *J. Phys. Chem.* **1996**, *100*, 12265.
(454) Kafafi, S. A. *J. Phys. Chem. A* **1998**, *102*, 10404.
(455) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.
(456) Tuma, C.; Boese, A. D.; Handy, N. C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3939.
(457) Dobson, J. F. *Int. J. Quantum Chem.* **1998**, *69*, 615.
(458) Hall, R. J.; Hillier, I. H.; Vincent, M. A. *Chem. Phys. Lett.* **2000**, *320*, 139.
(459) Engel, E.; Höck, A.; Dreizler, R. M. *Phys. Rev. A* **2000**, *61*, 032502.
(460) Le Barbu, K.; Brenner, V.; Millié, P.; Lahmani, F.; Zehnacker-Rentien, A. *J. Phys. Chem. A* **1998**, *102*, 128.
(461) Del Bene, J.; Jordan, M. J. T. *Int. Rev. Phys. Chem.* **1999**, *18*, 119.
(462) Liu, S.; Dykstra, C. E. *J. Phys. Chem.* **1986**, *90*, 3097.
(463) Scheiner, S. *Hydrogen Bonding: A Theoretical Perspective*; University Press: Oxford, 1997.
(464) Abramov, Yu. A. *Acta Crystallogr.* **1997**, *A53*, 264.
(465) Espinosa, E.; Molins, E.; Lecomte, C. *Chem. Phys. Lett.* **1998**, *285*, 170.
(466) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600.
(467) Legon, A. C.; Aldrich, P. D.; Flygare, W. H. *J. Chem. Phys.* **1981**, *75*, 625.
(468) Legon, A. C.; Aldrich, P. D.; Flygare, W. H. *J. Chem. Phys.* **1981**, *75*, 2126.
(469) Read, W. G.; Campbell, E. J.; Henderson, G.; Flygare, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7670. Read, W. G.; Campbell, E. J.; Henderson, G. *J. Chem. Phys.* **1983**, *78*, 3501.
(470) Read, W. G.; Flygare, W. H. *J. Chem. Phys.* **1982**, *76*, 2238.
(471) Shea, J. A.; Flygare, W. H. *J. Chem. Phys.* **1982**, *76*, 4857.
(472) Baiocchi, F. A.; Williams, J. H.; Klemperer, W. *J. Phys. Chem.* **1983**, *87*, 2079.

(473) Gord, J. R.; Garrett, A. W.; Bandy, R. E.; Zwier, T. S. *Chem. Phys. Lett.* **1990**, *171*, 443.
(474) Gotch, A. J.; Zwier, T. S. *J. Chem. Phys.* **1990**, *93*, 6977.
(475) Walters, E. A.; Grover, J. R.; White, M. G.; Hui, E. T. *J. Phys. Chem.* **1985**, *89*, 3814.
(476) Moore, D. T.; Oudejans, L.; Miller, R. E. *J. Chem. Phys.* **1999**, *110*, 197.
(477) Oudejans, L.; Miller, R. E. *J. Phys. Chem. A* **1999**, *103*, 4791.
(478) Herrebout, W. A.; Everaert, G. P.; van der Veken, B. J.; Bulanin, M. O. *J. Chem. Phys.* **1997**, *107*, 8886.
(479) Andrews, L.; Johnson, G. L.; Davis, S. R. *J. Phys. Chem.* **1985**, *89*, 1706.
(480) Gutowsky, H. S.; Arunan, E.; Emilsson, T.; Tschopp, S. L.; Dykstra, C. E. *J. Chem. Phys.* **1995**, *103*, 3917.
(481) Kollman, P.; McKelvey, J.; Johansson, A.; Rothenberg, S. *J. Am. Chem. Soc.* **1975**, *97*, 955.
(482) Pople, J. A.; Frisch, M. J.; Del Bene, J. E. *Chem. Phys. Lett.* **1982**, *91*, 185.
(483) Topiol, S.; Sapse, A. M.; Bunce, J. *Chem. Phys. Lett.* **1986**, *124*, 514.
(484) Araújo, R. C. M. U.; da Silva, J. B. P.; Ramos, M. N. *Spectrochim. Acta* **1995**, *51A*, 821.
(485) Hinchliffe, A. *Chem. Phys. Lett.* **1982**, *85*, 531.
(486) De Almeida, W. B.; Hinchliffe, A. *Chem. Phys.* **1989**, *137*, 143.
(487) Backsay, G. B.; Kerdraon, D. I.; Hush, N. S. *Chem. Phys.* **1990**, *144*, 53.
(488) Backsay, G. B. *Mol. Phys.* **1992**, *77*, 61.
(489) Lin, Z.; Bytheway, I. *Chem. Phys. Lett.* **1995**, *240*, 541.
(490) Clavero, C.; Durna, M.; Cledós, A.; Ventura, O. N.; Bertran, J. *J. Comput. Chem.* **1987**, *8*, 481.
(491) Kang, H. C. *Chem. Phys. Lett.* **1996**, *254*, 135.
(492) Tang, T. H.; Cui, Y. P. *Can. J. Chem.* **1996**, *74*, 1162.
(493) Menéndez, M. I.; Suárez, D.; Sordo, J. A.; Sordo, T. L. *J. Comput. Chem.* **1995**, *16*, 659.
(494) Sapse, A. M.; Jain, D. C. *J. Phys. Chem.* **1984**, *88*, 4970.
(495) Brèdas, J. L.; Street, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 7001.
(496) Tarakeshwar, P.; Lee, S. J.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **1998**, *108*, 7217.
(497) Salai Cheettu Ammal, S.; Venuvanalingam, P. *J. Chem. Phys.* **1998**, *109*, 9820.
(498) Chandra, A. K.; Nguyen, M. T. *Chem. Phys.* **1998**, *232*, 299.
(499) Herrebout, W. A.; van der Veken, B. J. *J. Am. Chem. Soc.* **1997**, *119*, 10446.
(500) Herrebout, W. A.; Lundell, J.; van der Veken, B. J. *J. Phys. Chem. A* **1999**, *103*, 7639.
(501) Fau, S.; Frenking, G. *Mol. Phys.*, **1999**, *96*, 519.
(502) Tarakeshwar, P.; Lee, J. Y.; Kim, K. S. *J. Phys. Chem. A.* **1998**, *102*, 2253.
(503) Tarakeshwar, P.; Lee, S. J.; Lee, J. Y.; Kim, K. S. *J. Phys. Chem. B* **1999**, *103*, 184.
(504) Tarakeshwar, P.; Kim, K. S. *J. Phys. Chem. A* **1999**, *103*, 9116.
(505) Andrews, A. M.; Taleb-Bendiab, A.; LaBarge, M. S.; Hillig, K. W., II; Kuczkowski, R. L. *J. Chem. Phys.* **1990**, *93*, 7030.
(506) Pranata, J. *Bioorg. Chem.* **1997**, *25*, 213.
(507) Rayón, V. M.; Sordo, J. A. *J. Chem. Phys.* **1999**, *110*, 377.
(508) Zoidis, E.; Dorfmüller, Th. *Chem. Phys.* **1995**, *196*, 171.
(509) da Silveira, N. P.; Rodembusch, F. S.; Pereira, F. V.; Samios, D.; Livotto, P. R. *Chem. Phys.* **2000**, *253*, 165.
(510) Marcus, R. A. *Adv. Chem. Phys.* **1999**, *106*, 1.
(511) Sutin, N. *Adv. Chem. Phys.* **1999**, *106*, 7.
(512) Bixon, M.; Jortner, J. *Adv. Chem. Phys.* **1999**, *106*, 35.
(513) Dessent, C. E. H.; Johnson, M. A.; Becker, I.; Cheshnovsky, O. *Adv. Chem. Phys.* **1999**, *106*, 265.
(514) *Electron Transfer-From Isolated Molecules to Biomolecules, Part I and II*; Prigogine, I., Rice, S. A., Bixon, M., Jortner, J., Eds.; John Wiley and Sons Inc.: New York, 1999.
(515) Schiedt, J.; Weinkauf, R.; Neumark, D. M.; Schlag, E. W. *Chem. Phys.* **1998**, *239*, 511.
(516) Maeyama, T.; Oikawa, T.; Seguchi, K.; Mikami, N. *J. Phys. Chem. A* **1997**, *101*, 8371.
(517) Hendricks, J. H.; Lyapustina, S. A.; de Clercq, H. L.; Snodgrass, J. T.; Bowen, K. H. *J. Chem. Phys.* **1996**, *104*, 7788.
(518) Desfrançois, C.; Abdoul-Carime, H.; Schermann, J. P. *J. Chem. Phys.* **1996**, *104*, 7792.
(519) Desfrançois, C.; Periquet, V.; Bouteille, Y.; Schermann, J. P. *J. Phys. Chem. A* **1998**, *102*, 1274.
(520) Choi, H. S.; Suh, S. B.; Cho, S. J.; Kim, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 12094. Oh, K. S.; Lee, C.-W.; Choi, H. S.; Lee, S. J.; Kim, K. S. *Org. Lett.* **2000**, *2*, 2679.
(521) Kim, K. S.; Oh, K. S.; Lee, J. Y. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 6373.
(522) Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1998**, *108*, 5151. Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1999**, *110*, 8429.

CR990051I