WORLD OF VAN DER WAALS SPECIES

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Van der Waals species (molecules, ions, radicals) attract the attention of chemists, chemical physicists and molecular biologists. Study of these systems presents a real challenge for both experimentalists and theorists. The main features of the contemporary possibilities for quantum chemical treatment are illustrated mostly on systems studied in the authors' laboratory. Prospects in the area are briefly outlined.

1. INTRODUCTION

For almost a century the science of chemistry was elaborated along purely inductive lines. The accumulated experimental observations were in due time transformed into the rules and laws of chemistry. The introduction of quantum, statistical, and classical mechanics into the realm of chemistry has permitted chemistry to be developed deductively, i. e. on the basis of the axioms of these physical disciplines.

It was only in the early seventies that the chemical community began to consider seriously the existence of intermolecular complexes, also called van der Waals (vdW) species. These species are the products of interactions between the permanent and instantaneous electric and magnetic multipoles. It is fortunate that vdW chemistry and physics had adequate theoretical tools available from the very beginning of their development, as it would not have been easy to elaborate vdW chemistry, or more specifically, rules governing structure and reactivity, based on experimental evidence alone, i.e. inductively. This article is a brief description of the results obtained in our laboratory in connection with structure elucidation and calculations of both the physical characteristics and the reactivities of vdW species.

2. SELECTION OF COMPUTATIONAL METHODS

We have repeatedly been able to describe the main lines for the selection of a proper computational procedure[1 – 4]. Strictly speaking, there are only two extreme possibilities. The more sophisticated alternative is based on the beyond Hartree–Fock–Roothaan (SCF) calculations. The electron correlation should be covered as completely as possible. Regardless of the method used for calculating the electron correlation energy (e.g., configuration interaction, CI, Møller–Plesset perturbation theory, MP, coupled-cluster method, CC), the SCF wave function must be obtained for a basis of at the least DZ or TZ type augmented by the polarization and diffusion functions. The interaction energy, ΔE, for the vdW system R . . . T (Eq. (*1*))

$$\mathrm{R} + \mathrm{T} \rightleftharpoons \mathrm{R}\ldots\mathrm{T}, \qquad \Delta E \tag{1}$$

consists of SCF and correlation (COR) energy contributions,

$$\Delta E = \Delta E^{\mathrm{SCF}} + \Delta E^{\mathrm{COR}} . \tag{2}$$

We have accumulated extensive evidence[3,4] that, at any computational level of calculation, it is always expedient to correct the calculated interaction energy for the basis set superposition error (BSSE).

Accurate calculations require the inclusion of tripleelectron excitations; thus it is necessary, e. g., with the MP method, to consider the fourth-order contributions. There exists some evidence[3,5,6] for the partial compensation of the MP third- and fourth-order contributions, so that satisfactory results can be obtained even at a relatively easily accessible MP2 level. Some extended systems, such as the benzene dimer of benzene...noble gas atom complexes, have been studied at this level. Needless to say, dozens of CRAY-YMP hours are necessary for these studies.

Before passing to the other extreme possibility, to empirical potentials, we will mention briefly two procedures enabling the theoretical study of much larger complexes. In the first one, the Hartree–Fock interaction energy is approximated by the SCF interaction energy obtained with the MINI-1 basis set corrected for the BSSE, and the interaction correlation energy is approximated using the dispersion energy calculated empirically by the London expression. The MINI-1 SCF interaction energy for neutral, as well as for ionic, vdW systems yields[7] geometries and stabilization energies comparable to those obtained from calculations with the 6-31G* basis set. The correlation interaction energy consists of inter- and intramolecular parts. The former term, which is always negative (stabilizing the vdW system), corresponds to the perturbation dispersion energy, and it could be approximated by the first term of the respective expansion, proportional to r^{-6}. The change in the intramolecular correlation energy (the latter term) is important when the dipole (quadrupole) moments evaluated at the SCF and beyond SCF level differ. This change is not dramatic for small systems, but for large dipolar systems, it may be important, and the correlation interaction energy may even be positive (destabilizing). Let us close this section by mentioning that the above combination of the SCF interaction energy and the London dispersion energy was also advocated by Kolos[8].

The second procedure makes use of the semiempirical methods of quantum chemistry. We have frequently had the opportunity to warn against the use of these methods in the realm of vdW species[3,4]. The recently introduced AM1 and PM3 semiempirical methods[9] are, however, better suited for the theoretical treatment of some types of vdW molecules. These methods were parametrized with respect to the H-bond characteristics, among others. It is certainly still (and obviously will remain) beyond the capabilities of these semiempirical methods to yield reasonable values of various characteristics for a majority of types of vdW molecules. However, for strong vdW molecules, especially for complexes with multiple H-bonds (e.g., DNA base pairs), these methods yield surprisingly good structures, stabilization energies and vibrational frequencies[10].

Van der Waals interactions play a fundamental role in several areas where even the smallest acceptable model systems include hundreds or thousands of atoms. Clearly, the only realistic approach in these cases is the use of empirical potentials. The use of standard empirical potentials is questionable, however. It is almost impossible to find a unique set of terms and parameters that reliably describe simultaneously strong, i. e. covalent (intramolecular), and weak intermolecular interactions. Perhaps the only currently available and acceptable approach relies on the combination of an empirical force field for the description of the intramolecular energy and a pair potential for the evaluation of the intermolecular energy[11,12]. The total energy, which is optimized, consists of intra- and intermolecular parts. The latter is expressed as the sum of the electrostatic, dispersion, and repulsion terms[12]:

$$E^{\mathrm{TOT}} = E^{\mathrm{INTRA}} + E^{\mathrm{INTER}} = E^{\mathrm{MM2}} + E^{\mathrm{ES}} + E^{\mathrm{D}} + E^{\mathrm{R}}, \qquad (3)$$

where E^{MM2} is the MM2 force field energy[13]. Only pair interactions are considered in the E^{ES}, E^{D}, and E^{R} terms. These terms are proportional to r^{-1}, r^{-6}, and r^{-40}, where r is the interatomic distance. The repulsion term is approximately equal to the hard-sphere repulsion. There are no adjustable parameters in the first and second terms; the E^{ES} utilizes the atomic charges calculated from the molecular electrostatic potential while the E^{D} is based on the experimental atomic polarizabilities and ionization potentials[12]. The only variable parameters are contained in the repulsion term and they have been obtained on the basis of the *ab initio* SCF interaction energies of model complexes.

It is also possible not to use any experimental value, but rather, to parametrize the empirical potential completely on the basis of theoretical interaction energies. In order fit the constants of the potential, a sufficiently extensive ensemble of *ab initio* interaction energies must be used. This procedure was first employed by Clementi[14]. Let us stress in this connection that it is necessary to use a reliable theoretical procedure, which in general means that the BSSE and correlation (or dispersion) energy term must be included. Additionally, there is another important point. An expression including the r^{-1}, r^{-6}, and r^{-12} terms is most frequently used as the potential. In the majority of instances this expression can be used for straightforward fitting of the *ab initio* interaction energies, which means that the constants associated with the individual terms are optimized simultaneously. The unpleasant consequence of this is that the physical significance of the individual terms (Coulomb, dispersion, and exchange repulsion terms) is not retained. In order to preserve their physical significance, it is necessary to parametrize the terms individually[15].

Having outlined various approaches, we will now describe the procedure to be followed to obtain a complete set of useful computational data for vdW molecules. In the first step, carefully selected parts of the P.E.S. are investigated at a sufficiently sophisticated level (e.g., MP2/DZ + P). These calculations yield the structure, geometry, and electric multipole moments. The second step involves refined calculations. For the minima obtained in the first step, calculations are carried out with larger basis sets and more correlation is included. Good-quality stabilization energies are obtained. In the third step, the constants of the empirical potential in 6–12 or 1–6–12 form are fitted to the potential energies obtained in the first step. The newly-obtained potential is used (the fourth step) in variational vibration calculations: the vibrational frequencies, zero-point energy, and stabilization enthalpy are obtained. In the fifth and final step, the empirical potential enables computer experiments of the MC or MD type. These calculations permit us to obtain information on the structures of 1 : 1 and 1 : *n* complexes, to describe their dynamic behavior, and to evaluate their thermodynamic characteristics.

3. FROM SMALL TO EXTENSIVE vdW SYSTEMS

In our laboratory we have traditionally been interested in a broad spectrum of vdW species. We have focused primarily on extensive systems of two types: (i) models of biologically active systems and (ii) large ensembles of small species (ions, molecules) for modelling gas-phase, as well as condensed media solvation. As with classical chemistry, even those interested in extensive systems require some knowledge of small systems for methodological reasons. More specifically, in order to elaborate and exploit simplified computational schemes, it is necessary to test them on systems whose size does not prohibit the use of sophisticated methods.

Experimental results from several laboratories have sparked our interest in medium-sized systems. For these reasons, systems possessing between three and many thousands of electrons have been investigated in our laboratory. Let us begin with small systems *I* and *II* (Chart 1).

The H_4^+ vdW ion *I* (C_{2v}) is stabilized[16] with respect to H_3^+ and $H^\bullet$ (MP4/6-31 + G*) by 2.4 kcal/mol. The $(H_2)_2$ system *II* has attracted attention for over twenty years. The mutual orientation of the subsystem has frequently been modelled using linear, rectangular, T-shaped, and/or rhombic structures[17]. It has been shown only recently that

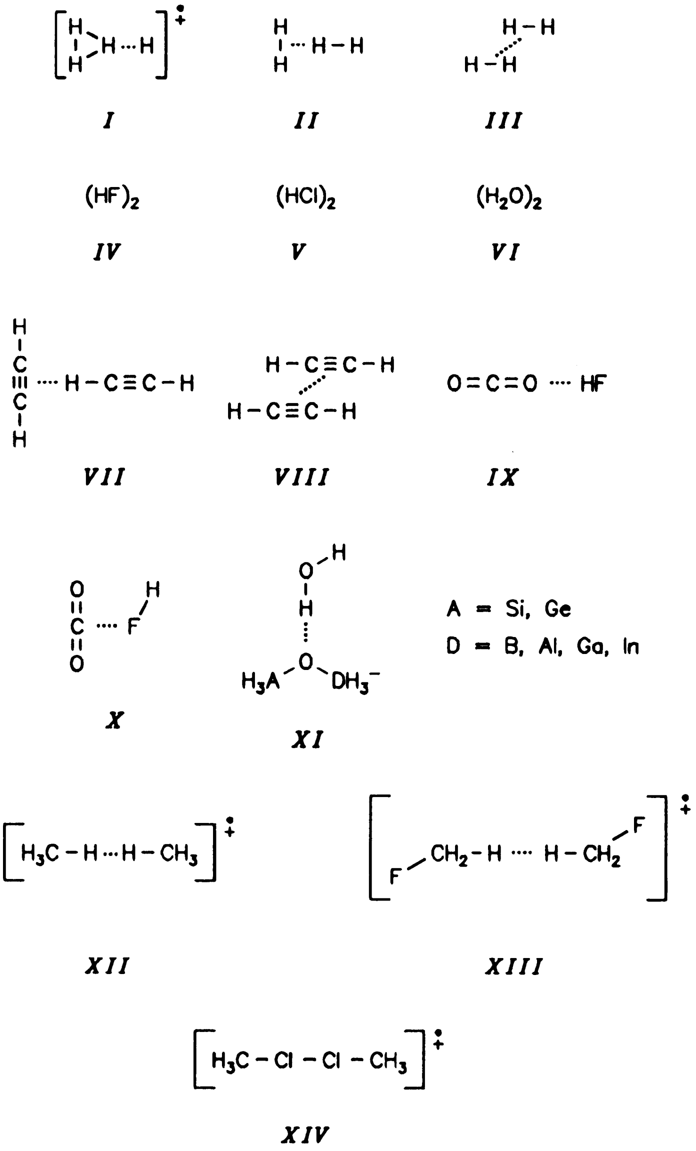

CHART 1

the T-shape represents the only minimum on the potential energy surface, while structure *III* is Eyring's activated complex. The T-shape is a consequence of the fact that a quadrupole–quadrupole interaction represents the major attractive term. Saddle point *III* separates two equivalent T-shaped minima. They can be distinguished by using labelling (with, e.g., deuterium). Some other products of quadrupole–quadrupole interaction follow the same pattern (e.g., the acetylene dimer, the benzene dimer, vide infra). The $(H_2)_2$ system has also been used to investigate the role of the basis set and of the BSSE. It has been shown[17] that the BSSE plays an important role with very large basis sets and it is especially important for ΔE^{COR}.

Various types of hydrogen-bonded molecules (*IV* – *XI*) have been studied. For hydrogen-bonded complexes *VII* and *IX*, two equivalent forms exist, separated by saddle points *VIII* and *X*. Complexes of type *XI* have been studied in connection with zeolite chemistry[18 – 20]. In addition to simple dimers of hydrides of the first and second row atoms (*IV* – *VI*, refs[21,22]) their radical cations and methyl derivatives have also been studied[23,24]. Linear $(CH_4)_2^+$ vdW system *XII* is worth mentioning[25] because it involves an H–H bond. A completely analogous system derived from CH_3F (*XIII*) was localized on the $C_2H_6F_2^+$ P.E.S. (ref.[23]). An analogous Cl-derivatives does not exist but its isomer containing a three-electron, two-center bond (*XIV*) is stabilized by 23 kcal/mol with respect to free CH_3Cl plus CH_3Cl^+ (MP2/6-31G**, ref.[24]).

Medium-sized complexes include species *XV* – *XX* in Chart 2. Benzene dimer *XVII*, the prototype for interactions between aromatic systems, had long been believed to possess a sandwich structure, until Klemperer's experiments[26] showed that the dimer is polar and excluded such a structure. Recent experiments in Schlag's laboratory[27] are consistent with the nearly T-shaped structure of the dimer. Our calculations[28] at the MP2/6-31 + G* level have shown that the T-shape corresponds to the minimum, but the potential around the minimum is extremely shallow. The wagging motion around the lowest hydrogen in the ±20° region is practically nonhindered. This finding, as well as the calculated dipole moment, agree with experiment. The same is true of the benzene . . . X complex, *XV*, with C_{6v} geometry[29]; the agreement between MP2 and experimental geometries is very good. Furthermore, the intermolecular frequencies for benzene . . . Ar and benzene . . . Kr, evaluated using potentials based on MP2 calculations, agree very well with the respective experimental values. However, for the stabilization enthalpy, the existing experimental data for the benzene dimer (1.6 ± 0.5 kcal/mol, ref.[30]) and benzene . . . Ar (0.4 ± 0.1 kcal/mol, ref.[30]) are significantly lower than the theoretical values (2.7 and 1.1 kcal/mol, respectively; zero-point energies were included). We have evidence[28,29] for compensation of the MP3 and MP4 terms for both complexes; the MP2 stabilization enthalpies are therefore rather accurate.

Our interest in analogous vdW molecules, including 1,2-benzyne (*XVI*), is connected with our attempts to interpret the vibrational spectra of benzyne formed photochemically in cavities of solid argon[31].

Both subsystems in *XVIII*, *s*-tetrazine and acetylene, possess acidic as well as basic centers. Initially, seven structures were studied[32]; the most stable one is indicated in Chart 2. The N-basicity of *s*-tetrazine is rather high; the stabilization energy for *XVIII* amounts to 14.7 kcal/mol.

Our investigation of the structure of a vdW intermediate in the interaction between the phenol radical cation and water is based on the vibrational frequencies, measured[33] for the intermediate. This work[34] has not yet been finished but the complex *XIX* is stabilized by 35 kcal/mol (MP2/3-21G*) with respect to $PhOH^+$ and H_2O.

Finally, in connection with a study of 10- and 12-vertex boranes[35], mononegative and neutral systems were also investigated; these systems include species like H, Li, or He (*XX*) in the centre of the borane cage. These systems might represent stable species but it is not yet clear whether a small particle can pass through the borane cage.

Let us pass to systems playing a role in molecular biology. The proper pairing of DNA bases (guanine (G), cytosine (C), adenine (A), thymine (T)) is essential for the functioning of the genetic code. All the possible 29 DNA base pairs were studied[36] using the *ab initio* SCF method (MINI-1 basis set) in combination with the London

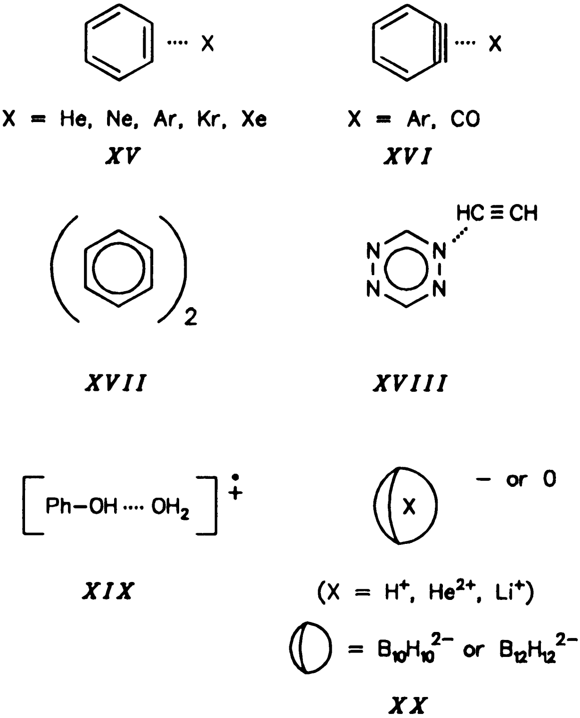

CHART 2

dispersion energy. Fair agreement has been obtained between the theoretical enthalpies and the experimental gas-phase enthalpies. The dispersion energy contribution is even more significant than expected; it is responsible for a very important part of the total stabilization energy. Moreover, it was found that the dispersion energy is not compensated (as stated repeatedly in the litarature) by the BSSE. The guanine–cytosine (GC) pair, having three H-bonds, is the most stable; its stabilization (26.5 kcal/mol) is larger than that of the adenine–thymine (AT) pair (16.0 kcal/mol). The stabilization energy in the cited study[36] was determined with a rigid subsystem. The effect of relaxation of the subsystem geometry was investigated by Hrouda et al.[10]. The gradient optimization of all the degrees of freedom of the AT pair (the Watson–Crick structure) increased the SCF stabilization energy from 10.3 kcal/mol (rigid subsystems) to 13.1 kcal/mol (taking into consideration the relaxation energy and BSSE). The difference is surprisingly small. Extension of the basis set (MIDI-1) resulted in only a small SCF stabilization energy increase (from 13.1 to 13.6 kcal/mol). It should be mentioned, however, that this calculation was performed at MINI-1 geometry.

Let us pass to extensive models of biomolecules. The interaction of a fragment of B-DNA, having 14 alternating GC pairs, and the flexible tripeptide Lys-Ala-Ala was studied[12] using an empirical procedure as described above (Eq. (*3*)). It was found that intramolecular relaxation of the peptide resulted in a considerable decrease in the total energy of the complex. Analysis of the individual energy terms suggests that the electrostatic term is responsible for the preferential binding of the peptide to a specific part of the DNA. The dispersion energy, which is less specific, contributes considerably to the overall stabilization. Its importance was also demonstrated for the interaction of tripeptide Lys-Ala-Ala with four different models of DNA (ref.[37]).

4. FITTING THE ANALYTICAL FUNCTION THROUGH THE NONEMPIRICAL *ab initio* INTERACTION ENERGY

The analytical function should be sufficiently flexible and should contain a manageable number of free parameters: the form of the function is based on the nature of the vdW forces acting between the subsystems. For example, for the benzene . . . Ar complex, the predominant stabilization comes from the dispersion energy, while repulsion is due to the exchange-repulsion energy. The former term is proportional to r^{-6}, the latter to r^{-12}. Hence, the resulting potential has the form

$$\varphi = -c_1 r^{-6} + c_2 r^{-12} . \qquad (4)$$

If the complex studied is additionally stabilized by electrostatic forces, the resulting potential should contain an electrostatic term which is proportional to r^{-1}. The resulting potential then assumes the following form

$$\varphi = c_3 r^{-1} - c_1 r^{-6} + c_2 r^{-12} . \qquad (5)$$

Fitting the empirical function to the nonempirical *ab initio* interaction energy could be carried out in one of two ways: (i) simultaneous fitting of all the terms to the nonempirical *ab initio* interaction energy; (ii) separate fitting of the repulsive and attractive terms of the potential to the different parts of the interaction energy (e.g., SCF interaction energy and MP2 correlation interaction energy). The latter procedure results in a parameter set having one important feature: the individual terms retain their original physical meaning. If all the terms are fitted simultaneously (the former procedure), it is meaningless to ascribe physical significance to the terms.

Benzene . . . Ar represents a model complex for which the accuracy and reliability of the various potentials can be tested[15,40]. Three potentials were used: (i) the 6–12 Lennard–Jones (L.–J.) potential, used in Jortner's laboratory[38], was adjusted to the heats of adsorption of rare gases on graphite; (ii) the Morse-type potential, used in our laboratory for evaluation of the vibrational frequencies, was adjusted to the MP2 P.E.S.; (iii) a general potential of the $r^{-m} - r^{-n}$ form, used in our laboratory primarily for molecular dynamics (MD) calculations, was also fitted to the MP2 P.E.S. These potentials are labelled as A, B, and C, respectively. Agreement among the intermolecular distances and stabilization energies, obtained with these potentials, is satisfactory (Table I). The high level of agreement between potential A and potentials B and C goes even further. The intermolecular stretching frequencies, obtained from the solution of the one-dimensional vibrational Schrödinger equation using potentials A, B, and C, amount to 42, 44, and 43 cm^{-1}, respectively. However, use of the full-dimensional vibrational Schrödinger equation results in rather different frequencies. The resulting stretching and bending frequencies are summarized in Table I. From this table it clearly follows that the stretching and bending modes evaluated with the MP2 potentials (B, C) agree well with the experimental data, unlike the frequencies evaluated with the 6–12 L.–J. potential (A). Furthermore MD calculations on benzene . . . (Ar)$_n$ (n = 1 – 9) with

TABLE I

Theoretical and experimental properties of the benzene . . . Ar complex: ΔE interaction energy in kcal/mol, R distance between centers of mass in 10^{-10} m, ν_s vibrational stretching frequencies in cm^{-1}, ν_b and ν_b' vibrational bending frequencies in cm^{-1}

Procedure	ΔE	R	ν_s	ν_b	ν_b'
6–12 L.–J. potential	1.12	3.48	33	22	22
MP2 calculation	1.23[a]	3.53[a]	37[b]	26[b]	26[b]
			40[c]	30[c]	29[c]
Experiment[d]		3.58	40	31	31

[a] Data from ref.[29]; [b] general type of potential, for details see text; [c] the Morse type of potential, for details see text; [d] data from ref.[39].

potential A and potential C revealed[41] important differences in the respective structures of single clusters, as a consequence of the different shape of the P.E.S.'s based on the 6–12 L.–J. potential and MP2 calculations.

5. CONCLUSIONS AND PROSPECTS

The chemistry and molecular physics of vdW species fascinate scientists for several reasons. Firstly, sophisticated treatment of these systems almost always presents a challenge to both experimentalists and theorists. Secondly, especially in the realm of biology, intermolecular forces frequently represent a kind of "electronic trigger in a powerful weapon". Thirdly, a deeper understanding of the physical behaviour and reactivity of molecules in condensed media cannot be attained without a greater and deeper understanding of noncovalent intermolecular interactions. Fourthly, it is very realistic to assume an overwhelming role for computer experiments of MC and MD types in all areas of the natural sciences in the coming years; again, real knowledge and the correct description of vdW interactions represent the *conditio sine qua non*. Finally, the world of vdW molecules is, in contrast to the world of common molecules, effectively infinite, and the architecture of a great many of them assumes a unique beauty.

As far as the future is concerned, even if the speed of computer progress remains unchanged, numerous topical medium-sized vdW species will probably not be accessible at a really sophisticated level by the end of the century, and this is not the only difficulty. Physically meaningful information frequently requires knowledge not only of quantum chemical but also of statistical mechanical characteristics. This is an additional reason why intense attention should be paid to the improvement of the algorithms used in computer experiments, MD in particular. This effort will be rewarding from the point of view of chemistry, molecular physics and biology only when the potential used is of really high quality.

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