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Theoretical Studies of van der Waals Molecules and Intermolecular Forces

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I. Introduction

Over the past 10 years, there have been major advances in experimental methods for observing van der Waals complexes, mostly by spectroscopic means. The resulting spectra contain a great deal of detailed information on intermolecular forces and have stimulated corresponding advances in the theoretical methods used for calculating intermolecular potential energy surfaces and for handling the dynamics of the complexes themselves. The purpose of this review is to describe the theoretical advances that have been made in the study of van der Waals complexes and the resulting advances in our understanding of intermolecular forces.

Various aspects of van der Waals molecules have been the subject of earlier reviews. Le Roy and Carley[1] described the determination of potential energy surfaces from the spectra of van der Waals molecules in 1980. Ab initio methods for calculating potential energy surfaces have been reviewed by Van der Avoird et al.[2] and Van Lenthe et al.,[3] and experimental studies of van der Waals spectra have been reviewed by Dyke[4] and by Legon and Millen.[5] Studies of predissociating states of van der Waals molecules have been reviewed by Beswick and Jortner,[6] by Le Roy,[7] by Gentry,[8] by Janda,[9] and by Celii and Janda.[10] A Faraday Discussion on van der Waals Molecules was held in Oxford in 1982,[11] and a NATO Advanced Research Workshop was held in Maratea, Italy, in 1986.[12]

For the purpose of the present review, we define a van der Waals molecule to be a complex formed in the gas phase (or in a molecular beam) between two stable neutral monomers. We thus exclude "chemically bound" floppy molecules such as N_2O_4 and species formed from ionic monomers such as KCN even though the dynamical methods used for such systems are in many ways similar to those used for van der Waals complexes. We also do not consider potentials for inert gas pairs in any detail, since these have recently been comprehensively reviewed by Aziz.[13]

In terms of the type of experimental data available, van der Waals complexes fall into two basic classes. For the simplest systems, such as complexes between atoms and diatomic and linear triatomic molecules, the experimental data are very detailed and are sensitive to a large part of the potential energy surface; for such systems, theoretical work has aimed at calculating the entire potential energy surface or at determining it from the experimental data. In a few cases, spectroscopic data on van der Waals complexes have been combined with data from other experiments (such as bulk gas properties or molecular beam scattering). For more strongly bound complexes, formed between pairs of polar molecules, the experimental data are generally restricted to the ground vibrational state and contain information on a small region of the potential in the region of its absolute minimum. For such systems, theoretical work has concentrated on rationalizing the equilibrium structures and properties of the complexes. Since the questions addressed by theory are quite different for these two classes of complex, they will be dealt with separately in the present review; however, it should be appreciated that advances in both experimental and theoretical methods are constantly extending the range of molecules for which complete potential energy surfaces can be determined, so that the

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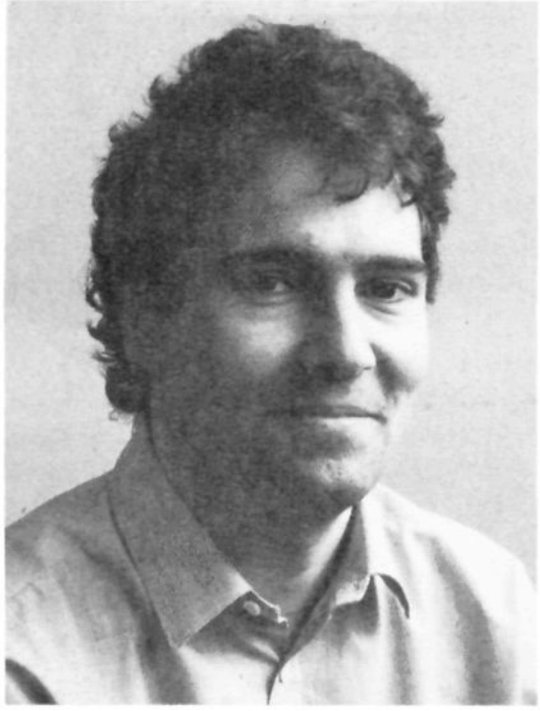
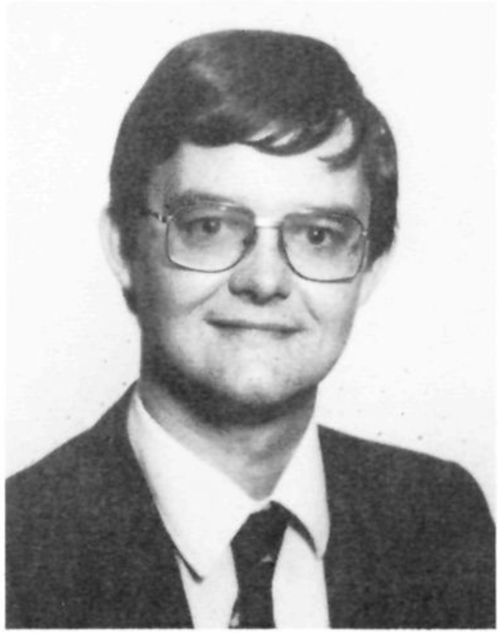


Patrick Fowler became a Lecturer in Chemistry at the University of Exeter in 1985, after 4 years of research in theoretical chemistry at Cambridge and a year at Durham. His Ph.D. thesis (Sheffield, 1980) was on "Vibration–Rotation Effects on Molecular Properties". Current research interests are in the general theory, calculation, and modelling of molecular properties, properties of ions in solids, van der Waals complexes, and bonding in cluster molecules.

boundary between the two classes changes with time.

The intermolecular potential between a pair of nonlinear molecules treated as rigid rotors is a function of six coordinates (the intermolecular distance and five angles). This number is reduced somewhat if atoms or linear molecules are involved; an atom–linear molecule complex requires two coordinates, while a linear-molecule dimer requires four. Conversely, if vibrational excitation (or relaxation) is important, then the number is increased by the number of vibrational coordinates included. The calculation or determination of a complete potential energy surface for larger systems is thus clearly a formidable task. This is another reason why both experimental and theoretical studies of larger complexes have concentrated on establishing equilibrium configurations and properties.



Jeremy Hutson received his B.A. from Oxford University in 1978, and continued to work there for his D. Phil. (1981), which was on the determination of anisotropic intermolecular forces from the spectra of van der Waals complexes. He subsequently spent 2 years as a NATO Postdoctoral Fellow at the University of Waterloo, Canada, working on photodissociation processes in van der Waals complexes and on molecular scattering theory. He returned to the UK as Drapers' Company Research Fellow and later Stokes Research Fellow at Pembroke College, Cambridge, working on the interpretation of atom–surface scattering experiments. Since 1987, he has been a Lecturer in Physical Chemistry at the University of Durham. His current research interests are in the determination of intermolecular potentials from experimental data of various kinds and in the dynamics of van der Waals complexes and adsorbates.

II. Representation and Partitioning of Intermolecular Potentials

As will be seen below, "brute force" ab initio methods of calculating intermolecular forces are both expensive and prone to underestimate some contributions (notably dispersion forces). However, the individual contributions to the interaction potential can be calculated much more cheaply and provide much more insight into the origin of the potential. Even when a potential has been calculated, it is usually necessary to fit the calculated points to a parametrized functional form, since it is not feasible to perform ab initio calculations at every intermolecular configuration required for dynamical calculations. Most recent theoretical work has thus concentrated on methods that partition the intermolecular potential V^{int} into contributions:

$$V^{\text{int}} = V^{\text{short}} + V^{\text{elec}} + V^{\text{ind}} + V^{\text{disp}} \qquad (1)$$

where the four terms are the short-range, electrostatic, induction, and dispersion contributions, respectively. The short-range term includes all "chemical" effects, including repulsive interactions, and decays exponentially with intermolecular distance. The electrostatic term takes account of the interaction between the permanent multipole moments of the monomers (and is thus zero if one monomer is a spherical atom). The induction term describes the effect of the polarization of the charge cloud of each monomer by the electrostatic field due to the other, and the dispersion term describes the interaction due to correlations of the fluctuating instantaneous multipoles of the two monomers; it is the only attractive interaction between closed-shell atoms. It should be noted that there can be additional terms contributing to the interaction energy for interactions involving excited atoms or molecules ("resonant dipole" interactions, etc.).

The expansion of eq 1 has its roots in the exchange perturbation theory of intermolecular forces.[14-19] At long range, where overlap between the molecular charge clouds is insignificant, the various terms can be defined unambiguously, but at shorter range any perturbative treatment gives a large number of terms and there is no unique partitioning; indeed, the very concept of the order of perturbation theory is not well defined when the full exchange symmetry of the problem is included.[16] The formulation of exchange perturbation theory proposed by Murrell and Shaw[14] and Musher and Amos[15] has been widely used, because it gives a convenient partitioning of the dispersion energy.[19]

An alternative partitioning of the interaction potential is

$$V^{\text{int}} = V^{\text{SCF}} + V^{\text{intra}} + V^{\text{disp}} \tag{2}$$

where V^{SCF} is the interaction energy evaluated from a self-consistent-field supermolecule calculation (see below), V^{intra} is the intramolecular correlation energy of the monomers (which, like the other terms, may depend on the intermolecular coordinates), and V^{disp} is again the dispersion energy arising from intermolecular electron correlation. From a purely operational point of view, it is necessary to arrive at prescriptions for estimating the various terms in eq 1 without performing detailed calculations in every case, and such prescriptions are necessarily approximate. For example, it is common practice to associate V^{SCF} with the sum of V^{short}, V^{elec}, and V^{ind}, so that the total interaction energy is given by

$$V^{\text{int}} = V^{\text{SCF}} + V^{\text{disp}} \tag{3}$$

The distance-independent part of the intramolecular correlation energy is absorbed in the supermolecule calculation, but eq 3 nevertheless neglects any dependence of the intramolecular correlation energy on the intermolecular coordinates, as well as various cross terms. It thus neglects the effect of intramolecular correlation on the repulsive potential (via changes in monomer charge densities and sizes) and on the electrostatic and induction potentials (via changes in monomer multipole moments and polarizabilities). Nevertheless, this approximation is at the heart of most of the semiempirical methods of calculating intermolecular forces, such as those of Douketis et al.[20] and Tang and Toennies.[21] There is some evidence that the neglected terms are small, at least for the atomic systems on which the semiempirical work has concentrated so far.

The remainder of this section will consider the work that has been done on representing the different contributions to intermolecular potentials and the functional forms that have been found appropriate for each type.

A. Short-Range Interactions

In an exchange perturbation formulation, the dominant term in the short-range potential, V^{short}, is the valence repulsion term, which arises from intermolecular Coulomb and exchange terms involving electrons on different monomers. The different formulations of exchange perturbation theory give slightly different definitions of this term, but to a first approximation it is proportional to the square of an overlap integral between orbitals on the two molecules.[17] Since the electronic wave functions decay exponentially with distance at long range, the valence repulsion is also quite well represented by exponentials in the intermolecular distance R, at least at long range. Such representations can be generalized, either by using a sum of exponentials with different exponents or by multiplying by a power of R, but this is usually not necessary if the other terms in the potential are represented accurately. There are in any case ambiguities in the definitions of the electrostatic, induction, and dispersion potentials at short range, and it is common practice to absorb any errors caused by inadequate representations of these into V^{short}. The major problem in representing short-range forces is the representation of the angle dependence, and the remainder of this subsection will concentrate on this aspect.

For weakly anisotropic systems, it is adequate to expand the potential directly in terms of an appropriate complete set of angular functions. Thus the short-range part of the rare gas–H_2 potentials (with the H_2 bond length frozen) can be written in the form

$$V^{\text{short}}(R,\theta) = \sum_{\lambda} A_{\lambda} \exp(-\beta_{\lambda} R) P_{\lambda}(\cos\theta) \tag{4}$$

where the functions $P_{\lambda}(\cos\theta)$ are Legendre polynomials.[22] A similar approach can be taken for the H_2 dimer,[23] but for larger molecules it breaks down. The difficulty can be seen most simply by considering the interaction between an atom and a hard ellipsoid (representing, for example, a CO_2 molecule). In this case, the potential for a particular value of R will be zero (or at least small) for most angles but will rise to infinity (or a large value) for angles where the atom and the ellipsoid intersect. Such a discontinuous potential cannot be expanded in a finite number of angular terms. The problem persists for real molecules, where the repulsive potential is of course softer; the expansion of $V^{\text{short}}(R,\theta)$ in terms of angular functions is often very slowly convergent, and the problem becomes increasingly serious for larger molecules.

The most satisfactory solution to this problem is to expand the *reference distance* and the exponent, rather than the potential itself, in terms of angular functions. Thus, in the atom–CO_2 case, the potential is expanded as

$$V^{\text{short}}(R,\theta) = A' \exp[-\beta(\theta)(R - R_{\text{ref}}(\theta))] \tag{5}$$

where

$$R_{\text{ref}}(\theta) = \sum_{\lambda} R_{\text{ref},\lambda} P_{\lambda}(\cos\theta) \tag{6}$$

$$\beta(\theta) = \sum_{\lambda} \beta_{\lambda} P_{\lambda}(\cos\theta) \tag{7}$$

Such expansions are generally much more quickly convergent than an angular expansion of the potential itself. For more complicated systems, involving more than one angular coordinate, the angular functions needed are more complicated, but the same idea can be applied.[24]

Equations 5–7 can describe molecules of any shape and make no a priori assumptions about the potential (except for the single-exponential approximation). However, for approximate work (or in the absence of more detailed information) an atom–atom additive model of the repulsive potential may be useful. In such a representation, the repulsive potential (or even the whole interaction potential) is written in the form

$$V^{\text{short}}(R,\theta) = \sum_{ij} V_{ij}^{\text{short}}(R_{ij}) \qquad (8)$$

where the pair potential $V_{ij}^{\text{short}}(R_{ij})$ between atoms i and j depends only on the distance R_{ij} between them and (for short-range interactions) may be taken to be a single exponential. Atom–atom additive potentials are a fairly severe approximation but offer obvious advantages; they are convenient, easy to evaluate for any particular intermolecular configuration, and offer some insight into the origin of the repulsive forces. Moreover, they can be used to estimate how the intermolecular potential varies as the monomers vibrate.[25] However, it should be noted that, where detailed tests have been possible, atom–atom additive models have *not* proved particularly accurate; and some atoms, notably hydrogen, make very different contributions to the repulsive potential, depending on their chemical environment.[26]

B. Electrostatic Interactions

The electrostatic energy, V^{elec}, of a pair of molecules is the energy of interaction between their permanent charge distributions. In the approximation that electron exchange between the subsystems is neglected, the electrostatic energy is the expectation value of the Coulomb interaction operator (the perturbation)[27]

$$V^{\text{elec}} = \frac{1}{4\pi\epsilon_0}\int \Psi_a^{(0)*}\Psi_b^{(0)*}\sum_{ij}\frac{e_i^{(\text{a})}e_j^{(\text{b})}}{R_{ij}}\Psi_a^{(0)}\Psi_b^{(0)}\,\mathrm{d}\tau_a\,\mathrm{d}\tau_{\text{b}} \qquad (9)$$

where $\Psi_{\text{a}}^{(0)}$ and $\Psi_{\text{b}}^{(0)}$ are the unperturbed ground-state wave functions of molecules a and b and R_{ij} is the distance between the ith charge $e_i^{(\text{a})}$ in a and the jth charge $e_j^{(\text{b})}$ in b. The integration is over the space of each molecule.

The interaction modifies the charge distribution of each monomer, but this contributes to the energy only at second and higher order. The electrostatic energy is first order in the Coulomb interaction and as such is pairwise additive. Given two wave functions, it is possible to evaluate the integral (9) directly. This is done in the methods that partition the SCF interaction energy.[28,29] Meath and co-workers[30] have used a partial-wave expansion of the first-order energy (9) to explore the effect of charge overlap on the electrostatic interaction in the N_2 dimer. However, it is not practical to perform such calculations for every possible separation and orientation, so that a functional form for the electrostatic energy is necessary.

If the separation between the monomers is large compared with their dimensions, a multipole expansion of the interaction Hamiltonian may be made and the energy expressed in terms of the permanent multipole moments of each monomer.[27] Classically, the multipole moments of an array of charges e_j are the Cartesian tensors

$$\xi^{(0)} = q = \sum_j e_j \qquad (10)$$

$$\xi_\alpha^{(1)} = \mu_\alpha = \sum_j e_j r_{j\alpha} \qquad (11)$$

$$\xi_{\alpha\beta}^{(2)} = \Theta_{\alpha\beta} = {}^1\!/\!_2\sum_j e_j(3r_{j\alpha}r_{j\beta} - r_j^{\,2}\delta_{\alpha\beta}) \qquad (12)$$

$$\xi_{\alpha\beta\ldots\nu}^{(n)} = (-1)^n\sum_j r_j^{\,2n+1}\nabla_\alpha\nabla_\beta\ldots\nabla_\nu\left(\frac{1}{r_j}\right) \qquad (13)$$

where q is the total charge, μ the dipole, Θ the quadrupole, etc. In quantum mechanics these become operator equations and the permanent moment is the expectation value of the corresponding operator. For some purposes a spherical tensor representation has advantages over the Cartesian forms.[31,32]

From the definition, eq 13, it is clear that each tensor is symmetric under permutation of subscripts. The moments are traceless, vanishing on contraction of any pair of indices (e.g., $\Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0$) and thus the moment of nth degree has up to $2n + 1$ independent components. Elements of molecular symmetry tend to reduce this number; for a spherical neutral atom all moments are zero, while for a linear molecule with the origin on the figure axis each tensor has at most one independent component. Only the first nonvanishing moment is independent of the choice of origin for the r_j. Thus, for a neutral polar molecule the dipole moment is independent of origin but the quadrupole moment is not.[27] All odd multipoles (dipole, octopole, ...) vanish for centrosymmetric molecules if the origin is chosen at the center.

The multipole expansion for the electrostatic energy of interaction of two molecules a and b is

$$\begin{aligned} V^{\text{elec}} = {} & Tq^{(\text{a})}q^{(\text{b})} + T_\alpha(q^{(\text{a})}\mu_\alpha^{(\text{b})} - q^{(\text{b})}\mu_\alpha^{(\text{a})}) + \\ & T_{\alpha\beta}\left(\frac{1}{3}q^{(\text{a})}\Theta_{\alpha\beta}^{(\text{b})} + \frac{1}{3}q^{(\text{b})}\Theta_{\alpha\beta}^{(\text{a})} - \mu_\alpha^{(\text{a})}\mu_\beta^{(\text{b})}\right) + \\ & \frac{(-1)^{n'}}{(2n-1)!!(2n'-1)!!}T_{\alpha\beta\ldots\nu\alpha'\beta'\ldots\nu'}\xi_{\alpha\beta\ldots\nu}^{(n)(\text{a})}\xi_{\alpha'\beta'\ldots\nu'}^{(n')(\text{b})} \end{aligned} \qquad (14)$$

where the T tensors are successive derivatives[33]

$$T = (4\pi\epsilon_0)^{-1}R^{-1} \qquad (15)$$

$$T_\alpha = (4\pi\epsilon_0)^{-1}\nabla_\alpha R^{-1} = -(4\pi\epsilon_0)^{-1}R_\alpha R^{-3} \qquad (16)$$

$$T_{\alpha\beta} = (4\pi\epsilon_0)^{-1}\nabla_\alpha\nabla_\beta R^{-1} = (4\pi\epsilon_0)^{-1}(3R_\alpha R_\beta - R^2\delta_{\alpha\beta})R^{-5} \qquad (17)$$

$$T_{\alpha\beta\ldots\nu} = (4\pi\epsilon_0)^{-1}\nabla_\alpha\nabla_\beta\ldots\nabla_\nu R^{-1} \qquad (18)$$

and R is the vector from an origin in molecule a to an origin in molecule b. Here and elsewhere, repeated Greek subscripts indicate summation over all three Cartesian components, and $n!! \equiv 1\cdot3\cdot5\cdot\ldots n$. The full energy is of course independent of choice of origin but truncation of the multipole series at some finite n leads to a spurious origin dependence.

More seriously, the multipole expansion is not strictly convergent at any separation; it is an asymptotic series in R^{-1}.[34] Methods for the summation of such series exist[35] and may be accurate at large separations where overlap of the unperturbed charge clouds is negligible. However, to give useful results at the distances characteristic of van der Waals complexes, improved convergence is necessary. One way to achieve this is by a distributed multipole analysis (DMA)[36,37] of the molecular charge distribution. In Stone's DMA method an ab initio charge density is described by sets of charges, dipoles, quadrupoles, and so on located at a number of sites in the molecule, usually atoms and bond centers. The point multipoles are determined in a way that can be regarded as an extension of Mulliken population analysis. The convergence properties of the distributed multipole expansion have been discussed in detail by Stone and Alderton.[37] They conclude that DMA gives a description of electrostatic interactions that is accurate at all energetically accessible distances, including at the "surface" of a molecule as defined by the van der Waals radii. DMA also gives a detailed picture of qualitative features of the charge distribution; atomic dipoles and quadrupoles represent lone and bonding pairs, while π bonds lead to quadrupoles at bond centers. The expression for the electrostatic energy (9) can be applied to arrays of multipoles by summing over all pairs of sites with one in molecule a and the other in b.

Central multipoles of low order are available from experiment for many molecules; the dipole moment is measured by using the Stark effect[38] and the quadrupole moment (for nondipolar molecules) by measuring field-gradient-induced birefringence[39] or (for dipolar molecules) through first- and second-order Zeeman splittings.[40] For small molecules they may be calculated with useful accuracy by ab initio techniques. Typically an SCF calculation might be expected to overestimate a dipole moment by about 0.1 D.[41] Atomic multipoles may be obtained by fitting to experimental total multipoles[42] but for molecules that are not too large an ab initio DMA calculation is the method of choice; an option to do this is implemented in the CADPAC ab initio package.[43] Other ab initio schemes for obtaining distributed multipoles have been put forward by McLean (unpublished work quoted in ref 37) and by Cooper and Stutchbury.[44] Atomic multipoles can also be simulated by arrays of suitably placed point charges.[45-47]

Inside the molecular charge cloud no multipole expansion can converge to the correct limit for V^{elec}. The effects of penetration of charge clouds may be calculated by comparing the exact integral expression (9) with its expanded form.[48] It is usual to absorb these terms (which may be attractive) into the short-range "SCF repulsion".

C. Induction Interactions

The induction energy, V^{ind}, results from the interaction of the induced electric moments of each molecule with the permanent charge distribution of its partners.[33] Since it is caused essentially by a relaxation of charge clouds, it is always negative for molecules in their ground states and thus produces an attractive intermolecular force. The induction energy is rarely the predominant source of attraction between molecules and can often be neglected in comparison to the electrostatic and dispersion energies.

At second order of perturbation theory the induction energy for a pair of molecules a and b is[33]

$$V^{\text{ind}} = (4\pi\epsilon_0)^{-1}\left[\int \Psi_{\text{a}}^{(0)*}\Psi_{\text{b}}^{(0)*}\sum_{ij}\frac{e_i^{(\text{a})}e_j^{(\text{b})}}{R_{ij}}\Psi_{\text{a}}^{(0)}\Psi_{\text{b}}^{(1)}\,\mathrm{d}\tau_{\text{a}}\,\mathrm{d}\tau_{\text{b}} + \int \Psi_{\text{a}}^{(0)*}\Psi_{\text{b}}^{(0)*}\sum_{ij}\frac{e_i^{(\text{a})}e_j^{(\text{b})}}{R_{ij}}\Psi_{\text{a}}^{(1)}\Psi_{\text{b}}^{(0)}\,\mathrm{d}\tau_{\text{a}}\,\mathrm{d}\tau_{\text{b}}\right] \tag{19}$$

where $\Psi_{\text{a}}^{(1)}$ is the first-order change in the wave function of molecule a induced by the (nonuniform) electrostatic field of molecule b. Since the presence of further molecules would change this first-order wave function *and* add terms to the Coulomb interaction operator, the induction energy is not pairwise additive.

The induction or "polarization" energy may be evaluated from ab initio wave functions for a pair of molecules with a given separation and mutual orientation.[28,29] It is usual to replace $\Psi^{(1)}$ in the integrals (19) by sum-over-states expressions in these calculations. As with the electrostatic energy, however, it is necessary to represent the induction energy as a function of the monomer properties if progress is to be made.

The induction energy results from the distortion of a molecule by the electric field due to the charge distributions of its neighbors. In the long-range limit a Taylor expansion of this field can be made, using the value of the field and its gradients at some convenient origin in the molecule. For the pair of molecules a and b the induction energy is[33]

$$V^{\text{ind}} = -\frac{1}{2}\alpha_{\alpha\beta}^{(\text{a})}F_{\alpha}^{(\text{b})}F_{\beta}^{(\text{b})} - \frac{1}{3}A_{\alpha,\beta\gamma}^{(\text{a})}F_{\alpha}^{(\text{b})}F_{\beta\gamma}^{(\text{b})} - \frac{1}{6}C_{\alpha\beta,\gamma\delta}^{(\text{a})}F_{\alpha\beta}^{(\text{b})}F_{\gamma\delta}^{(\text{b})}\ldots - \frac{1}{2}\alpha_{\alpha\beta}^{(\text{b})}F_{\alpha}^{(\text{a})}F_{\beta}^{(\text{a})} - \frac{1}{3}A_{\alpha,\beta\gamma}^{(\text{b})}F_{\alpha}^{(\text{a})}F_{\beta\gamma}^{(\text{a})} - \frac{1}{6}C_{\alpha\beta,\gamma\delta}^{(\text{b})}F_{\alpha\beta}^{(\text{a})}F_{\gamma\delta}^{(\text{a})}\ldots \tag{20}$$

where $\alpha^{(\text{a})}$, $A^{(\text{a})}$, $C^{(\text{a})}$... are the dipole, dipole–quadrupole, and quadrupole polarizabilities, respectively, of molecule a and $F_{\alpha}^{(\text{a})}$, $F_{\alpha\beta}^{(\text{a})}$... are the static field and field gradient arising at an origin in b and caused by the charges in a. The higher polarizabilities A, C... depend on the choice of origin, and one must use the field and field gradient evaluated *at that origin.* This expression may be used directly[49] if the polarizabilities are known from experiment or calculation. Alternatively the fields themselves may be written as expansions in the permanent multipole moments. Formulas for the electric fields of multipolar molecules are tabulated by Price et al.[50]

Charge overlap effects may modify induction energies at short range. Knowles and Meath[51-53] have used partial-wave expansions of the integrals (17) to evaluate damping functions for the induction energy in He–HF and Ne–HF; for separations in the region of the van der Waals minimum and beyond, rather small deviations from the long-range interaction energies were found.

As might be expected from our discussion of the electrostatic energy, improved convergence for the fields and field gradients in the induction energy may be achieved by using distributed multipoles to represent the charge distribution that is the source of the field. It is also advantageous to distribute the *response* of a molecule to these fields, in other words to distribute the polarizability. A scheme for distributed polarizability analysis (DPA) of coupled Hartree–Fock wave functions has been proposed and implemented by Stone.[54] In it a molecule is represented by an array of sites, each of which carries a set of polarizabilities calculated by a partition of the perturbed wave function. The method by which these are obtained is somewhat more complicated than the multipole analysis and so far has been programmed only for linear arrays of sites. The method is of particular importance in modeling induced dipole moments in van der Waals complexes,[55,56] where, as is described later, it is very successful.

The induction energy is not pairwise additive, because the energy of a single molecule is quadratic in the field of the rest of the system. Further nonadditivity comes from the higher order perturbation energies or "back-induction" terms. Because the molecules are polarizable, their induced moments depend on the field they experience, which in turn depends on the total (induced + permanent) moments of their neighbors. To determine the total induction energy for N interacting molecules requires self-consistent solution of a set of N coupled equations.[57-60] Similar considerations apply to the induced moments themselves.[56]

D. Dispersion Interactions

The theory of dispersion forces between pairs of molecules is less well understood than that of electrostatic and induction forces, particularly in the region of the van der Waals minimum, where overlap of the molecular charge clouds is important. However, since dispersion forces make an important contribution to the intermolecular potential for nearly all systems and are the dominant attractive forces between nonpolar molecules, it is essential to model them as accurately as possible. The following discussion will concentrate on atomic systems, since they have been most extensively studied, but many parts of it may be extended to molecular systems, albeit with a considerable increase in algebraic complexity.

The dispersion energy between a pair of spherical atoms at long range may be written in the form

$$V^{\text{disp}} = \sum_{n=6}^{\infty} C_n R^{-n} \tag{21}$$

For atomic interactions, there are no odd-order terms in the potential before $C_{11}R^{-11}$ if relativistic (retardation) effects are neglected. Equation 21 may be generalized to handle interactions between molecules of arbitrary symmetry.[33,61,62] At short range, however, this behavior is modified, and the true dispersion energy (unlike eq 21) does not become infinite at $R = 0$. The dispersion energy must therefore be represented as a damped dispersion series

$$V^{\text{disp}} = \sum_{n=6}^{\infty} C_n R^{-n} D_n(R) \tag{22}$$

The dispersion coefficients C_n and the damping functions $D_n(R)$ are implicitly functions of the relative orientations and internal vibrational coordinates of the monomers. The damping functions are unity at long range but fall to zero at $R = 0$. They take account of the effects of overlap and finite size of the charge distributions and also correct for various other short-range terms. Early damping functions[63-65] simply removed the singularity in the dispersion potential at short range. However, if intermolecular electron exchange effects are neglected, it is possible to perform ab initio calculations of damping functions by evaluating the dispersion energy in a nonexpanded form.[66] Several general functional forms have been proposed[20,21] to represent the results of these calculations. Much of the earlier work was reviewed in ref 21, although Knowles and Meath have since extended the ab initio calculations to larger systems containing Ne, Ar, and HF.[51-53] Their calculations yield the dispersion energy in the form of a partial-wave expansion and can be used to determine damping functions by comparison with the asymptotic expressions. A similarly direct approach to the calculation of dispersion energies has been proposed by McWeeny,[67] and calculations using this formalism have been published for He_2 and the HF dimer.[68]

The most widely used damping functions are the HFD (Hartree–Fock dispersion) damping functions of Douketis et al.[20] and the incomplete Γ function damping functions of Tang and Toennies,[21] both of which ensure that the dispersion energy remains finite at short range. The HFD damping functions are of the form

$$D_n(R) = f(R) g_n(R) \tag{23}$$

where

$$f(R) = 1 - (\rho R)^{1.68} \exp(-0.78\rho R)$$

$$g_n(R) = [1 - \exp(-2.1 n^{-1} \rho R - 0.109 n^{-1/2} \rho^2 R^2)]^n$$

The functions $g_n(R)$ were fitted to ab initio damping functions, and $f(R)$ was added to take account of additional damping due to exchange effects.[20] The incomplete Γ function damping functions are[21]

$$D_n(R) = P(n + 1, \beta R) = 1 - \exp(-\beta R) \sum_{m=0}^{n} \frac{(\beta R)^m}{m!} \tag{24}$$

where $P(n + 1, \beta R)$ is an incomplete Γ function as defined by Abramowitz and Stegun.[69] The length scaling factor ρ in the HFD damping function is generally taken from ratios of monomer ionization energies,[20] whereas the analogous parameter β in the Tang–Toennies functions is generally set equal to the exponent used for the repulsive potential (see section IIA). However, when fitting to experimental data, these scaling factors are perhaps best viewed as disposable parameters.

Most of the work on damping dispersion forces has been on atomic systems, and much less is known about molecular systems. As mentioned above, Knowles and Meath have recently performed ab initio calculations on systems containing HF, but there is not yet sufficient information to give reliable prescriptions for molecules in general. Various ad hoc schemes have been used, based on the atom–atom damping functions described above. Rodwell and Scoles[70] used the HFD damping functions for rare gas–H_2 systems, with separate values of ρ for each term in a Legendre expansion of the potential, while Fuchs et al.[71] allowed ρ to be an explicit function of the angle θ for He–N_2. Douketis et al.[72] used a site–site representation of the dispersion energy for Ar–HCl and Ar–HF, with different values of ρ for the different sites. These are all sensible approaches, but none is definitive; much more work is needed to establish the best method of damping for molecular systems.

Dispersion Coefficients

The successful use of semiempirical methods requires reliable values of the dispersion coefficients C_n. These may be obtained in several ways, and each has its advantages and drawbacks. This section describes the sources available for dispersion coefficients, and attempts to delineate their strengths and weaknesses.

The long-range dispersion interaction between a pair of spherical atoms may be written (in atomic units) using second-order perturbation theory[73]

$$V^{\mathrm{disp}} = -\sum_{l_a=1}^{\infty}\sum_{l_b=1}^{\infty}\frac{2}{\pi}\frac{2(2l_a+2l_b)!}{4(2l_a)!(2l_b)!}\int \alpha_{l_a}{}^{a}(i\omega)\alpha_{l_b}{}^{b}(i\omega)\,\mathrm{d}\omega\, R^{-2(l_a+l_b+1)} \qquad (25)$$

where $\alpha_{l_a}{}^{a}(i\omega)$ is the 2^{l_a}-pole dynamic polarizability of atom a, evaluated at imaginary frequency $i\omega$. The dynamic polarizabilities have poles on the real frequency axis but are smooth monotonically decreasing functions along the imaginary axis. Each C_n coefficient in the dispersion series may thus be written in terms of integrals over imaginary frequency

$$C_6{}^{ab} = \frac{3}{\pi}\int \alpha_1{}^{a}(i\omega)\alpha_1{}^{b}(i\omega)\,\mathrm{d}\omega \qquad (26)$$

$$C_8{}^{ab} = \frac{15}{2\pi}\int [\alpha_1{}^{a}(i\omega)\alpha_2{}^{b}(i\omega) + \alpha_2{}^{a}(i\omega)\alpha_1{}^{b}(i\omega)]\,\mathrm{d}\omega \qquad (27)$$

$$C_{10}{}^{ab} = \frac{14}{\pi}\int [\alpha_1{}^{a}(i\omega)\alpha_3{}^{b}(i\omega) + \alpha_3{}^{a}(i\omega)\alpha_1{}^{b}(i\omega)]\,\mathrm{d}\omega + \frac{35}{\pi}\int \alpha_2{}^{a}(i\omega)\alpha_2{}^{b}(i\omega)\,\mathrm{d}\omega \qquad (28)$$

though it should be noted that there are additional contributions to C_{11} and higher order coefficients due to perturbation terms beyond second order. Most of the methods available for calculating dispersion coefficients rely, at least implicitly, on evaluating eq 26–28 using some approximate representation of the functions $\alpha_l(i\omega)$ for the monomers concerned.

The most general method for obtaining the $\alpha_l(i\omega)$ is to evaluate them directly from ab initio calculations. It should be stressed that the calculations required are on the monomers involved; they are *not* supermolecule calculations and are thus relatively inexpensive. Once an SCF calculation of the monomer wave function has been performed, it is relatively straightforward to perform coupled Hartree–Fock (CHF) calculations to determine polarizabilities.[74] The ability to do this is a standard option in the CADPAC ab initio package,[43] and the calculations are feasible for moderately large monomers. The random phase approximation (RPA), which is also sometimes used, is equivalent to the CHF approach. Calculations of dynamic polarizabilities have been published for several monomers that form important van der Waals molecules.[75] Quite large and flexible basis sets are required to give reliable results, but this presents no great difficulty. The usual practice is to evaluate $\alpha_l(i\omega)$ on a grid of ω values chosen to be the abscissas of an appropriate Gaussian quadrature,[75] so that evaluating the integrals over ω for any pair of monomers is straightforward.

It is at first sight surprising that monomer calculations at the SCF level are able to give useful values for dispersion coefficients, since the dispersion energy itself arises entirely from electron correlation. However, it is the *intermolecular* correlation that gives the dispersion energy, and dispersion coefficients obtained from coupled Hartree–Fock calculations are usually accurate to better than 10%. However, if it is necessary to go beyond this, the situation is at present less satisfactory. Established methods exist for calculating static polarizabilities from wave functions incorporating configuration interaction (CI),[76,77] but methods for dynamic polarizabilities are still under development.[78] Nevertheless, it is likely that the near future will see considerable advances in this area and that calculating dynamic polarizabilities and dispersion coefficients from correlated monomer wave functions will become routine.

An alternative approach to the problem of determining dispersion energies is to use experimental information on oscillator strength distributions. In practice, this gives accurate values only for C_6 coefficients, since only the dipole oscillator strengths can be measured accurately. The dynamic polarizabilities may be written[73]

$$\alpha_l(\omega) = \sum_n \frac{f_n{}^l}{E_n{}^2 - \omega^2} \qquad (29)$$

where $f_n{}^l$ is the oscillator strength for the 2^l-pole transition from the ground state to state n, and E_n is the corresponding transition energy. The summation in eq 29 implicitly includes integration over the ionization continuum. The oscillator strengths $f_n{}^l$ necessarily obey certain sum rules. Defining

$$S_l(k) = \sum_n f_n{}^l E_n{}^k \qquad (30)$$

the Thomas–Reiche–Kuhn sum rule specifies that $S_1(0)$ must be equal to N, the number of electrons in the molecule, while $S_l(-2)$ is by definition the static multipole polarizability $\alpha_l(0)$. The form of eq 29 immediately suggests that $\alpha_l(i\omega)$ might sensibly be approximated by a single-term Padé approximant

$$\tilde{\alpha}_l(i\omega) = \frac{\alpha_l(0)\eta_l{}^2}{\eta_l{}^2 + \omega^2} \qquad (31)$$

where η_l is an effective excitation energy. Tang[79] has shown that if η_l is taken to be the lowest excitation energy for 2^l-pole radiation, the approximate $\tilde{\alpha}_l(i\omega)$ is everywhere smaller than the true value $\alpha_l(i\omega)$; conversely, if η_l is chosen to be $[S_l(0)/\alpha_l(0)]^{1/2}$, $\tilde{\alpha}_l(i\omega)$ is everywhere greater than $\alpha_l(i\omega)$. Thus if $\alpha_l(i\omega)$ is represented by eq 31 with these choices for η_l, integrating eq 26–28 yields lower and upper bounds to the dispersion coefficients C_n. The integrals obtained may actually be performed analytically for this form of $\tilde{\alpha}_l(o\omega)$

$$\int \tilde{\alpha}_{l_a}{}^{a}(o\omega)\tilde{\alpha}_{l_b}{}^{b}(i\omega)\,\mathrm{d}\omega = \frac{\pi\alpha_{l_a}{}^{a}(0)\alpha_{l_b}{}^{b}(0)\eta_{l_a}{}^{a}\eta_{l_b}{}^{b}}{2(\eta_{l_a}{}^{a} + \eta_{l_b}{}^{b})} \qquad (32)$$

If additional oscillator strength sums are used as input data, tighter bonds may be obtained by extending eq 31 to include two or three terms. Details of this approach have been given by Tang, Norbeck, and Certain,[80] who used it to obtain upper and lower bounds to C_6, C_8, and C_{10} coefficients for rare gas and alkali metal atom pairs. More recently, Standard and Certain[81] have presented updated values, using improved input data for the oscillator strength sums; there are some significant differences between the two sets of numbers, and it should be emphasized that the "bounds" obtained in this way are reliable only if the input data (static polarizabilities and oscillator strength sums) are accurate.

A somewhat different approach has been developed by Meath and co-workers[82–92] and has been applied to a wider range of atomic and molecular species. They use experimental values of oscillator strengths and electron inelastic scattering cross sections to evaluate explicit dipole oscillator strength distributions (DOSDs), constraining the DOSDs to satisfy the Thomas–Reiche–Kuhn sum rule and to reproduce refractivity and dispersion measurements for the relevant dilute gases.[82] The DOSDs may then be used to evaluate dispersion coefficients.[83] The complete DOSDs are very voluminous, and the quantities actually reported in the literature are sums $S_1(k)$ as defined by eq 30 and the additional sums $L_1(k)$ defined by

$$L_l(k) = \sum_n f_n{}^l E_n{}^k \ln E_n \qquad (33)$$

Approximate values for $C_6{}^{ab}$ may be obtained by using eq 26 and 32 with $\eta_1 = \exp(L_1(-2)/S_1(-2))$, and this usually gives results within 1% of the values obtained with the DOSDs directly.[82] An alternative approach, adopted in some of the most recent work,[89-92] is to represent the DOSDs by discrete "pseudo-DOSDs", which are specified as m pairs of effective oscillator strengths $\tilde{f}_i$ and excitation excitation energies $\tilde{E}_i$ such that $S_1(k)$ is represented correctly for $k = 2, 1, 0, ..., 3 - 2m$. This provides a compact representation of the DOSDs and is effectively equivalent to writing $\alpha_1(i\omega)$ as a sum of m terms of the type (31), so that once again the integrals required for the dispersion coefficients can be evaluated analytically. DOSDs have been determined for a wide range of atoms and molecules, including the rare gases and hydrogen halides,[92] H_2, N_2, O_2, NO, N_2O, NH_3 and H_2O,[82,83,89] CO and CO_2,[91] SO_2, CS_2 and OCS,[84] CH_4,[85,89] and various alkanes,[86,90] alkenes,[87] and alcohols.[88] The principal drawback of the method is that it is restricted to isotropic dipole properties and cannot provide information either on the anisotropy of dispersion forces or on higher order multipole properties such as C_8 and C_{10}.

For mixed interactions, useful approximations to dispersion coefficients can often be obtained from combination rules. If only the like–like dispersion coefficients $C_n{}^{aa}$ and $C_n{}^{bb}$ are known, the mixed dispersion coefficient $C_n{}^{ab}$ is sometimes taken to be the geometric mean, $(C_n{}^{aa}C_n{}^{bb})^{1/2}$. However, if the static polarizabilities are also known, rather better approximations are possible. This is most straightforward for C_6 coefficients: for each monomer, $C_6{}^{aa}$ and $\alpha_1{}^a(0)$ may be used to define an effective excitation energy $\eta_1{}^a$ from eq 26 and 32, and the resulting approximants for $\tilde{\alpha}_1{}^a(i\omega)$ and $\tilde{\alpha}_1{}^b(i\omega)$ may then be used to calculate $C_6{}^{ab}$. The resulting combination rule is[79]

$$C_6{}^{ab} = \frac{2C_6{}^{aa}\alpha_1{}^a(0)C_6{}^{bb}\alpha_1{}^b(0)}{C_6{}^{aa}[\alpha_1{}^b(0)]^2 + C_6{}^{bb}[\alpha_1{}^a(0)]^2} \qquad (34)$$

Similar but more involved expressions can be obtained for higher order dispersion coefficients by approximating the higher order dynamic polarizabilities in the same way, and the corresponding expressions for atom–diatom systems have been given by Fuchs et al.[71]

TABLE I. Slater–Kirkwood Parameters for Some Simple Atoms and Molecules

	$\alpha_1(0)$	C_6	η_1	N_{eff}
H	4.500	6.499	0.428	0.824
He	1.385	1.458	1.013	1.422
Ne	2.669	6.383	1.195	3.810
Ar	11.08	64.3	0.698	5.404
Kr	16.79	129.6	0.613	6.309
Xe	27.16	285.9	0.517	7.253
H_2	5.428	12.11	0.548	1.630
N_2	11.74	73.39	0.710	5.918
O_2	10.59	62.01	0.737	5.756
NO	11.52	69.78	0.701	5.662
N_2O	19.70	184.9	0.635	7.950
CO	13.08	81.4	0.634	5.264
CO_2	17.51	158.7	0.690	8.340
CH_4	17.27	129.6	0.579	5.797
NH_3	14.56	89.08	0.560	4.570
H_2O	9.642	45.37	0.651	4.082
HF	5.601	19.0	0.808	3.652
HCl	17.39	130.4	0.575	5.748
HBr	23.74	216.6	0.512	6.234

It is sometimes necessary to approximate dispersion coefficients without any information beyond the static polarizabilities of the monomers. Under these circumstances, London's formula or the Slater–Kirkwood expression may be used for C_6; the latter corresponds to the identification $\eta_1 = [N/\alpha_1(0)]^{1/2}$. Although N is nominally the number of valence electrons, this choice tends to overestimate C_6 by up to 20%; it is generallly better to choose N to be an effective number of electrons taken from the known behavior of some chemically similar species; N_{eff} is given in terms of $\alpha_1(0)$ and C_6 by

$$N_{eff} = \frac{16C_6{}^2}{9[\alpha_1(0)]^3} \qquad (35)$$

A list of values of $\alpha_1(0)$, C_6, η_1, and N_{eff} for some simple molecules is given in Table I.

The methods described above can usually be used to obtain reasonable values of $C_6{}^{ab}$ and $C_8{}^{ab}$ for the interaction of interest, but obtaining accurate values of the higher order coefficients is difficult, particularly for larger molecules. Even ab initio calculations present great difficulties for coefficients beyond C_8, since basis functions with high orbital angular momenta are needed to model higher order multipole polarizabilities. Nevertheless, values of C_{10}, C_{12}, etc. are needed when constructing semiempirical potentials; it is conventional to truncate the series at C_{14} or C_{16}, and omitting lower order terms can have significant effects. Thakkar and Smith[93] have shown that the relationship

$$\frac{C_{10}}{C_8} = \frac{49}{40}\frac{C_8}{C_6} \qquad (36)$$

derived using a simple oscillator model, holds quite well for real systems. Douketis et al.[20] extended this model to higher order coefficients, obtaining

$$\frac{C_{12}}{C_6} = \frac{17280}{16807}\left(\frac{C_{10}}{C_8}\right)^3 \qquad (37)$$

$$\frac{C_{14}}{C_8} = \frac{818741}{839808}\left(\frac{C_{12}}{C_{10}}\right)^3 \qquad (38)$$

These expressions also work well for the H–H and He–He interactions. Tang and Toennies[21] used the somewhat simpler form

$$\frac{C_{n+4}}{C_{n-2}} = \left(\frac{C_{n+2}}{C_n}\right)^3 \qquad (39)$$

Any errors in the lower order coefficients are magnified in the higher order coefficients, though the overall effect on the potential may be small.

Dispersion forces suffer from the same convergence problems at short range as electrostatic and induction forces, and a single-center angular expression can be very poorly convergent for large molecules. However, no detailed formulation of a distributed model for dispersion forces is available, and there are formal problems with such a formulation because distributed polarizabilities need to be nonlocal. Nevertheless, it seems intuitively reasonable to suppose that dispersion forces can be approximated by atom–atom pairwise models, and there is evidence that polarizabilities (and DOSDs) can be represented as a sum of contributions from functional groups.[94] In the absence of more detailed information, partitioning the dispersion energy into atom–atom contributions, using coefficients obtained from (for example) partitioned DOSDs,[95] seems to be a reasonable way of estimating dispersion energies involving larger molecules.

In summary, the method of choice for determining dispersion coefficients is to perform ab initio calculations. At present, possible exceptions to this are the inert gas pairs and isotropic C_6 coefficients for systems where dipole oscillator strength distributions (DOSDs) are available. However, ab initio calculations are likely to become even more advantageous in the future; computer time is becoming less expensive, and ab initio packages are becoming more powerful and more widely available. In addition, ab initio methods are the only ones capable of giving information on the dependence of dispersion coefficients on relative orientation and internal vibrational coordinates, and this information will become more important in the years to come.

III. Simple Systems: Complete Potential Energy Surfaces

A. Ab Initio Calculations

Most of the ab initio calculations that have been performed on van der Waals complexes have been so-called supermolecule calculations; that is, separate ab initio calculations are performed on the complex and on the individual monomers, and the interaction energy is evaluated by simply subtracting the monomer energies from the supermolecule energy. Supermolecule calculations on van der Waals complexes may be divided into two classes. Calculations at the self-consistent field (SCF) level are straightforward and computationally relatively inexpensive but fail to take account of correlation effects; since the dispersion energy, which dominates the attractive part of the potential for many simple systems, is itself a correlation effect, SCF calculations by themselves are inadequate for many purposes. However, as will be seen below, it is possible to make semiempirical corrections to account for the correlation energy. There are also various methods that calculate the correlation energy directly; examples of these are configuration interaction (CI) and perturbation theory calculations in various guises. These are much more expensive than SCF calculations and, except for the very smallest systems, have difficulty in recovering the whole of the dispersion energy. It is also more difficult to correct for the missing part of the dispersion energy than for the whole dispersion energy, since it is more difficult to formulate exactly what contributions have been omitted.

The most successful direct correlated calculations of an intermolecular potential are those of Meyer et al.[96] on He–H_2; they performed very detailed CI calculations with a large basis set, separating the intersystem correlation (dispersion) from the SCF and intrasystem correlation terms. Their potential has been shown by Schaefer and Köhler[97] to give good agreement with a wide range of experimental data for He–H_2 and He–HD mixtures. For larger systems, however, the situation is rather less satisfactory. Diercksen and co-workers[98,99] performed CI calculations on He–CO, including all single and double excitations explicitly and correcting for some quadruple excitations, while Billing et al.[100] performed many-body perturbation theory (MBPT) calculations on He–NH_3. Banks et al.[101] calculated the intermolecular potential for He–N_2 using the correlated electron pair approximation (CEPA) but obtained a potential well that was substantially too shallow. Approaches based on valence bond (VB) theory have also been proposed: Raimondi[102] has used a MO–VB method to calculate a potential energy surface for He–HF, and Gallup and Gerratt have proposed a variation–perturbation method,[103] which they have applied to Ne–HF. Unfortunately, in the cases where it has been possible to test these potentials against experimental data, they have invariably proved to be too shallow. In addition, there has been little work on systems containing atoms heavier than He. While He systems are important for bulk properties and in astrophysical contexts, they are generally very weakly bound, and spectroscopic measurements of van der Waals complexes containing He are sparse.

Basis Set Superposition Error

In the supermolecule method the interaction energy is calculated as a difference in total energy between the complex and the separated monomers. This has obvious numerical disadvantages. Coulson compared it to weighing a ship's captain by weighing the ship with and without him on board (see Kutzelnigg's expanded version of this comparison in ref 104). However, the method is popular because it is seemingly straightforward and requires no extra programming. The supermolecule approach also has several deeper advantages: it treats the whole potential surface uniformly, does not suffer from convergence problems (as in perturbation methods), and gives a proper treatment of intermolecular exchange effects (the Pauli principle). However, the method has a major drawback. At the end of the 1960s, it was realized that interaction energies calculated in this way include a spurious attractive contribution—the basis set superposition error (BSSE)— which arises because the monomers are stabilized in the complex, not for any physical reason, but simply because the basis functions on one monomer add flexibility to the basis set on the other. In the enlarged dimer basis set the monomers have lower energies. For weak complexes and small basis sets the BSSE can dominate the calculated interaction potential and, since it is easily mistaken for physical charge transfer,[49,105] can distort our picture of the nature of the forces between the monomers.

It is usual to correct for BSSE by the counterpoise method of Boys and Bernardi,[106] in which monomer energies are calculated in the full dimer basis. For each point on the potential surface the energy of a monomer is calculated in the presence of the basis functions (but not the electrons and nuclei) of its partner in the same position and orientation as in the dimer. The result obtained is usually an improvement[107] (in that it is closer to experiment) and the corrected energy is a smoother function of basis set size[108,109] (but see ref 110 for a counterexample).

Although the counterpoise method is widely used, it has been the subject of some criticism. It is often argued that in the dimer calculation the occupied orbitals of one monomer are not available to the electrons of the other and that therefore the Boys–Bernardi prescription might overestimate the "true" BSSE.[111] Corrected counterpoise schemes using only the virtual molecular orbitals of the partner have been proposed.[110,112,113] Although the concept of a true error is elusive, it should be noted that a corrected scheme is essential in certain cases, e.g., in calculating BSSE effects on the polarizability of an anion in a lattice, where the presence of point charges leads to unrealistically large corrections with the conventional method.[114]

Recent papers by Gutowski et al.[115,116] and a review by Van Lenthe et al.[3] argue that the most consistent results are obtained by using the *full* counterpoise correction for van der Waals dimers, both at SCF and correlated levels. They reject the "overestimation" criticisms of the full counterpoise correction, claiming that these rest on a misinterpretation of the role of the Pauli principle. They point out that, although the problem is not of great practical importance in SCF calculations on small systems where sufficiently large basis sets can be used, BSSE is still a significant problem in correlated calculations even on systems as small as He_2. A similar conclusion is reached by Szczesniak and Scheiner in their Møller–Plesset calculations on the water dimer.[109] This study also mentions a secondary cause of error. Quite apart from the effect of ghost orbitals on the monomer *energy*, basis set superposition causes changes in the monomer electrical properties, such as dipole moment and polarizability.[49,117] For example, in Ne–HF the Ne atom has a spurious dipole if its wave function is calculated in the full dimer basis. The altered properties have a secondary effect on the computed total energy and thus on the apparent interaction energy. The spurious electrostatic and induction energies can be removed by using long-range expressions.[49] This ignores penetration effects[109] but for the separations characteristic of van der Waals complexes is likely to give a useful approximation to this small contribution to BSSE. Some authors[117,118] take the view that this secondary form of BSSE is to be welcomed in calculations of dispersion energy, where it gives large multipole polarizabilities for relatively small basis sets. Latajka and Scheiner[119] have studied primary and secondary BSSE at the SCF and MP2 levels for the strong complexes Li^+–NH_3 and Li^+–H_2O. They reject the suggestion that secondary BSSE improves the interaction energy in general.

A further sophistication of the counterpoise technique has been suggested for calculations involving polar monomers. Loushin et al.[120] use a *polarization counterpoise correction* (pcc) (not to be confused with methods of the same name described in ref 110 and 113, which are essentially variants of the counterpoise scheme, omitting contributions from occupied orbitals and including those from ghost polarization functions) in which the energy of monomer A is evaluated *both* in the *full* dimer basis *and* in the presence of an array of point charges that simulate the electric field of monomer B. This is claimed to give a more accurate representation of the monomer in the complex, though the authors note that with a very large basis set the presence of point charges might lead to spuriously large corrections (cf. remarks in ref 114 on diffuse ions in point-charge lattices). If a more accurate representation of the electric field became desirable, a distributed multipole analysis[36] of the partner's charge cloud could be used instead of the array of point charges. The new pcc scheme[120] can be seen within the long-range theory of intermolecular forces as an attempt to correct for BSSE in the electrostatic and induction energies. For the HF dimer in a range of bases from 4-31G up to a doubly polarized triple-zeta set, pcc appears to give a good estimate of the BSSE in the hydrogen-bond energy, as measured against near-Hartree–Fock results.[120]

To the nonspecialist, the continued debate about the best form of the counterpoise correction may seem rather arid and technical. Indeed, as computer resources improve we can look forward to calculations with very large basis sets that are essentially free of BSSE and need no correction. For small systems at the SCF level this is already possible[115] but at the correlated level even He_2 is likely to require a counterpoise correction for some time to come.

Many post-SCF supermolecule methods suffer from a further complication: lack of size consistency. In a truncated CI expansion, the limiting energy of a well-separated supermolecule is not exactly equal to the sum of the monomer energies. This problem and its solution have been discussed in a review on weakly bound complexes by Van Lenthe et al.[3]

B. Empirical Potentials

Ultimately, the test of a calculated potential energy surface or of a potential model is how well it reproduces experimental results for the complex (or collision system) concerned. Purely ab initio potentials, by their very nature, have no adjustable parameters, so that they cannot be modified in any obvious way to fit experimental data. Purely empirical potentials, on the other hand, have the required flexibility to fit experimental data but often fail to satisfy the necessary theoretical constraints on the true potential. One of the major advantages of the semiempirical ansatz is that potentials constructed in this way can be constrained to have the theoretically correct behavior at long range and at short range, yet still have adjustable parameters that can be determined from experimental data in order to give the correct behavior in the theoretically intractable "intermediate region" around the potential minimum; the higher order dispersion coefficients and the length scaling factors in the dispersion damping functions are obvious candidates for treating in this way.

Types of Experimental Data

There are a wide variety of experiments that contain information on intermolecular potentials and that can be used to determine them. However, it is comparatively rare for any one experiment to contain enough information to determine the potential over the whole region of configuration space of interest, and simultaneous analysis of several properties is usually necessary.

Microwave spectra of van der Waals molecules provide a very valuable starting point for a potential surface determination and are available for a large number of complexes. They may be measured either in molecular beams or (for more strongly bound complexes) in bulk gas mixtures; molecular beam spectra usually involve only the lowest vibrational state of the complex (because of the very low effective temperatures in a molecular beam) whereas bulk gas spectra may contain "hot bands" corresponding to vibrationally excited states of van der Waals stretching or bending modes. This work has been reviewed quite recently[5] and will not be repeated here.

The nature of the information contained in microwave spectra depends to some extent on the type of complex being studied. The primary observables are of course the rotational constants, which contain information on the equilibrium structure; however, it should be remembered that a molecule has at most three rotational constants (only two of which are independent for a planar molecule) so that a single isotopic species does not give enough information to determine the complete molecular structure even for the simplest complexes. The approximation usually made is that the monomer structures are unchanged on complex formation, so that only the intermolecular distances and angles have to be determined from the spectra. Information on average bond angles may also be available from properties such as dipole moments and nuclear quadrupole coupling constants; for near-rigid complexes, these average angles are similar to the equilibrium angles. If microwave spectra for several different isotopic species can be measured, it is often possible to determine the "structure" uniquely; however, such an approach is valid only for near-rigid complexes and should be regarded with some suspicion for very weakly bound complexes (such as those containing rare gas atoms) since such species exhibit wide-amplitude bending and stretching motions that are likely to change quite significantly on isotopic substitution.

The microwave spectra do not contain any less information for highly nonrigid molecules, but a naive interpretation in terms of a single structure should be avoided. For such systems, indeed, additional spectroscopic constants may contain valuable information on the intermolecular potential. For atom–molecule complexes, for example, the dipole moment of the complex is usually dominated by the projection of the dipole of the monomer onto the inertial axes of the complex, and the measured dipole contains information on the expectation values of the intermolecular angles involved. Similarly, for complexes containing quadrupolar nuclei, nuclear quadrupole coupling constants contain information on different expectation values of the angles (since the quadrupole moment is a second-rank tensor, whereas the dipole moment is a first-rank tensor). It should be noted, however, that the angular information is essentially concerned with *expectation values*, and its interpretation requires a detailed dynamical calculation using the complete potential energy surface; it should *not* be interpreted in terms of an equilibrium structure except for near-rigid complexes.

Infrared spectra of van der Waals complexes are also extremely valuable; indeed, McKellar and Welsh's infrared spectra of Ar–H_2 in the region of the H_2 stretching fundamental[121] allowed the determination of the first reasonably accurate atom–molecule potential energy surfaces more than a decade ago.[122] However, complexes containing H_2 are rather special, since the lines are widely spaced (and therefore easily resolved) and the monomer spectrum is very weak. It is only in the past 5 years that it has become possible to obtain rotationally resolved vibrational spectra of more typical complexes such as Ar–HCl and $(HF)_2$. Methods now exist for measuring near-infrared spectra of van der Waals molecules both in molecular beams[123,124] and in bulk gases.[125] Such spectra are particularly valuable when they include combination bands in which a van der Waals bending or stretching mode is excited at the same time as a monomer fundamental vibration, since the frequencies of the van der Waals modes contain particularly unambiguous information on the potential surface; this information is generally complementary to that provided by microwave spectra and relates to regions of the potential away from the equilibrium geometry.

Similar information can be obtained from far-infrared spectra, in which the van der Waals modes are excited directly, rather than in combination with monomer fundamental modes. Indeed, far-infrared spectra are easier to interpret, since they relate to the potential surface for interaction of monomers in their ground vibrational states, whereas near-infrared spectra give information mostly on interactions involving vibrationally excited monomers. However, techniques for obtaining far-infrared spectra of complexes are in their infancy; Marshall et al.[126] and Saykally and co-workers[127–130] have recently obtained spectra of several bands of Ar–HCl using laser Stark resonance spectroscopy in a molecular beam, with fixed-frequency far-infrared lasers; such spectra can provide the most detailed information available so far on intermolecular potentials in the well region, but the experimental search and assignment problems are still considerable. The development of techniques using tunable far-infrared lasers will make this approach much more generally applicable.

Of course, spectroscopic methods are not the only ones that can provide information on intermolecular forces; indeed, they played a relatively minor role in the development of accurate potential curves for inert gas pairs.[13] All the classical bulk gas properties, such as second virial coefficients and viscosity and diffusion coefficients,[131] can be brought to bear on molecular systems. Mixed second virial coefficients are more difficult to measure than those of pure gases but are available for a fairly wide range of systems;[132] they may readily be calculated from a trial intermolecular potential, although quantum corrections may be required for light monomers at low temperatures.[131,133] In qualitative terms, second virial coefficients at low temperatures contain information on the volume of the potential well, whereas those at high temperatures contain information on the repulsive wall of the potential. It is possible to invert second virial coefficients directly[134,135] to obtain an effective one-dimensional potential curve, even for molecule–molecule systems.[136] There has been a considerable amount of work on how such effective potentials should be interpreted;[137–139] they are certainly *not* in general the same as the spherical average of the full potential.

Transport properties may also be measured for gas mixtures, and they too can be inverted to obtain an effective one-dimensional potential curve.[140,141] For weakly anisotropic systems, the effective potential obtained is very similar to that obtained by inverting virial coefficients,[137] but this is not true for strongly anisotropic systems.[138] However, the calculation of transport properties from a full potential energy surface is much less straightforward than for second virial coefficients. An exact calculation requires full quantum-mechanical (close-coupling) scattering calculations[142,143] for a wide range of collision energies, followed by averaging over the Maxwell–Boltzmann velocity distribution and the molecular rotational states. Such calculations are very expensive and have only been performed for a few simple systems.[97,144–149] Even for systems as simple as He–N_2, close-coupling calculations are only just computationally feasible,[149] and it is necessary to resort to approximation schemes. Decoupling methods such as the coupled states (CS) and infinite order sudden (IOS) approximations[142,143,150,151] have been widely used, as have classical schemes such as the Mason–Monchick approximation[152] or full classical trajectory calculations.[153–154] Semiclassical methods have also been developed.[155] The circumstances under which these approximations are or are not adequate are now beginning to be understood.

In addition to transport properties, there are a wide range of relaxation processes that can occur in molecular systems but not in atomic systems. These contain information on the anisotropy of the intermolecular potential, particularly in the repulsive region. Important relaxation properties[156] include sound absorption, the pressure broadening of spectroscopic lines, nuclear magnetic relaxation, and depolarized Rayleigh light scattering. Each of these properties can be characterized by a (temperature-dependent) effective cross section. Methods for calculating these cross sections from intermolecular potentials have been developed;[156] they involve the same scattering calculations as are required for the calculation of transport properties, and the same approximation schemes can be applied,[142,143] although with varying degrees of success for the different properties.

An additional potential source of information on anisotropic interactions is provided by the Senftleben–Beenakker effects (SBE), which are the effects of electric and magnetic fields on transport properties. These effects are very small but can be measured by differential techniques.[157] They depend on the orientation of molecules by the applied field and are nonexistent for spherical interactions; in principle, they too contain information on the anisotropy of the interaction. The SBE are each characterized by two cross sections, a "production" cross section, which determines the magnitude of the effect, and a relaxation cross section, which determines the field strength needed to saturate it. Methods for calculating SBE cross sections fall into the same theoretical framework as those for calculating transport and relaxation cross sections and involve scattering calculations;[142] however, in practice, it has been found that the approximate methods that work reasonably well for transport and relaxation cross sections fail completely for production cross sections,[151] so that extracting their information content has proved difficult.

Molecular beam scattering data can also yield valuable information on intermolecular potentials. The classical techniques used for atomic collisions[158] can be applied to molecular systems and provide total cross sections, summed over the initial and final internal states of the molecules. Techniques are also available for measuring state-to-state inelastic cross sections, either by time-of-flight techniques[159] or by using state-selective detection methods.[160] Under favorable circumstances, elastic and inelastic differential cross sections can be inverted directly to obtain an anisotropic potential.[161] However, this procedure requires very high quality experimental data and has not yet been widely applied. In general, total cross sections provide information mostly on the spherical part of the interaction potential, whereas inelastic cross sections provide information on the anisotropy. Nevertheless, some information on the anisotropy can be obtained from the damping of quantum oscillations in either differential or integral cross sections. For collisions with small reduced mass (such as those involving He atoms), the differential cross sections are dominated by diffraction oscillations, and the damping of these is principally sensitive to anisotropy in the repulsive wall of the potential; for larger reduced masses, diffraction oscillations are difficult to resolve, and rainbow oscillations are important; these too are damped by anisotropy, but in this case the damping is most sensitive to anisotropy in the well depth.[162]

The areas of applicability of the different types of measurement are to a large extent complementary. Molecular beam scattering measurements are at their best for systems containing He (or H_2) but are more difficult when both collision partners are heavy. Conversely, spectroscopic studies of van der Waals molecules are generally possible only for species which do *not* contain He, since He complexes are very weakly bound. Measurements of virial coefficients are possible for most systems, but the potential information contained in them is highly averaged. Transport and relaxation properties can also be measured for many systems, but extracting their information content is often expensive, especially for heavier molecules.

The procedures generally used for extracting potential information from the various experiments are also rather different. The spectra of van der Waals molecules are relatively inexpensive to calculate from a trial potential energy surface, so that with spectroscopic data it is often possible to carry out an automated least-squares fit to the experiment, including a statistical analysis of the residual errors. Potentials based on spectroscopic data can thus have well-defined uncertainties and confidence limits associated with them. Unfortunately, such a treatment has not yet been possible with scattering data; the procedure that has been followed is simply to vary potential parameters by hand, using physical intuition, until a potential that gives reasonable agreement with experiment is obtained. The problem with this approach, of course, is that it does not address the question of whether the potential thus obtained is uniquely determined by the experimental data or whether it is simply one of a large family of potentials capable of fitting the data. Transport properties are even more expensive to calculate than scattering data, so that the same problem applies a fortiori to them.

Specific Systems

There is now a fairly wide range of simple systems for which complete potential energy surfaces have been determined, with varying degrees of reliability. These include the interactions of inert gases with H_2, HCl, HF, N_2, O_2, CO_2, CH_4, and SF_6. There has also been some work on molecule–molecule systems such as the HF dimer, the C_2H_4 dimer, and the N_2 dimer.

The inert gas–H_2 systems have for a long time been the preeminent prototype systems for atom–molecule intermolecular forces, and this remains true. As mentioned above, the He–H_2 system is the only atom–molecule system for which a satisfactory pure ab initio potential exists. For the heavier inert gas–H_2 complexes, however, the spectroscopic and scattering data are of sufficient quality to allow the determination of uniquely detailed potential energy surfaces, including the dependence on the H_2 vibrational coordinate (bond length). The Ar–H_2 potential, in particular, has gone through several cycles of refinement as more and better experimental data became available. The potential was originally determined by Le Roy and van Kranendonk[122] and by Dunker and Gordon[163] on the basis of partially resolved near-infrared spectra obtained by McKellar and Welsh.[121] Subsequently, Le Roy and Carley[1] obtained improved potential energy surfaces based on the same experimental data by constraining the potentials to satisfy theoretical constraints based on calculations of the C_6 dispersion coefficient and the (independently known) He–Ar potential. The preferred potential of ref 1, the $BC_3(6,8)$ potential, was shown to give quite good results for the scattering of a beam of oriented H_2 molecules from Ar[164] and for various transport properties of Ar–H_2 mixtures.[147] However, it was subsequently shown that it did not reproduce either the nuclear hyperfine spectrum of the van der Waals complex[165–167] or the rotationally inelastic scattering of D_2 from Ar.[168,169] In addition, McKellar remeasured the near-infrared spectra of Ar–H_2 and Kr–H_2 in low-temperature gas mixtures at much higher resolution.[170] Le Roy and Hutson[171] therefore performed a combined least-squares fit to all these data, using a more recent form of the dispersion damping function, to determine new three-dimensional potential energy surfaces. The resulting surfaces (designated $TT_3(6,8)$ surfaces) are fairly similar to the older potentials of Le Roy and Carley,[1] but with smaller uncertainties, although the dependence of the potential anisotropy on the H_2 vibrational coordinate $\xi = (r - r_0)/r_0$ is significantly weaker than for the older potentials. The new Ar–H_2 potential also gives a satisfactory account of the total differential cross sections[168] and the mixed second virial coefficients[172,173] and has been used to calculate various transport and relaxation cross sections for Ar + H_2 mixtures.[148,174] $TT_3(6,8)$ potentials have also been determined for Kr–H_2 and X–H_2,[171] although for these systems molecular beam scattering data are not available.

The inert gas–H_2 potentials are actually very nearly isotropic and so do not make good prototypes for intermolecular forces in general. The inert gas–HCl potentials are more anisotropic and have also been the subject of a great deal of work; once again the Ar system is the best understood, but fairly good potentials are also available for Ne–HCl, Kr–HCl, and Xe–HCl. The first realistic potential to be determined for Ar–HCl was obtained by Holmgren et al.[175] (HWK potential) on the basis of the microwave and radiofrequency spectra of the van der Waals complex.[176,177] The quantities fitted were the rotational and centrifugal distortion constants of Ar–HCl and Ar–DCl and angular expectation values $\langle P_1(\cos\theta)\rangle$ and $\langle P_2(\cos\theta)\rangle$ obtained from the dipole moment and nuclear quadrupole coupling constants, respectively. The resulting potential was quite well determined in the region of the absolute minimum, which is at a linear Ar-H-Cl geometry. However, the HWK potential was very different from potentials determined from the pressure broadening of HCl rotational spectra,[178,179] and itself failed to reproduce the observed line-broadening data.[179] Accordingly, Hutson and Howard[180] performed a simultaneous least-squares fit to the microwave spectra, the line-broadening data, and the mixed second virial coefficients[181] and obtained the M3 potential; this was quite similar to the HWK potential near the minimum but had a considerably more anisotropic repulsive wall, allowing it to model the line-broadening data. The experimental data were not adequate to determine the potential around the linear Ar-Cl-H geometry, and the M3 potential was constrained to be featureless (without a secondary minimum) in that region.

Subsequently, Hutson and Howard[182] carried out similar work on the Ne–HCl potential, for which the microwave spectra *were* sufficient to determine the potential over the complete angular range, and found that in this case there was a secondary minimum near the linear Ne-Cl-H geometry. They therefore proposed similar potentials (designated M5 potentials)[182] for Ar–HCl, Kr–HCl, and Xe–HCl, constrained to have secondary minima at the linear inert gas–Cl-H geometry. Various semiempirical and ab initio calculations also found a secondary minimum at this geometry for Ar–HCl.[72,183,184] Buck and Schleusener[185] found that the Ar–HCl M5 potential was superior to the M3 potential in reproducing their measured total differential cross sections for Ar–HCl.[186] Measurements of the near-infrared spectrum in the region of the HCl stretching fundamental[187] also gave results in reasonably good agreement with the M5 potential. However, a definitive answer to the question of the presence or absence of the secondary minimum had to await the measurement of far-infrared spectra. This has recently become possible: Marshall et al.[126] have measured the spectrum of the Π bending state of Ar–HCl, and Saykally and coworkers have measured the Π bending[127,128] as well as the Σ bending[129] and stretching[130] modes. Comparison of these results with calculations of the M3 and M5 potentials[188] shows conclusively that there *is* a secondary minimum at the linear Ar-Cl-H geometry. The new spectra have now been used to determine an improved potential for Ar–HCl.[189]

Similar work has been carried out on Ar–HF, Kr–HF, and Xe–HF, although the experimental data are not as extensive as for the inert gas–HCl systems. Experimental microwave spectra of the complexes[190,191] were fitted to obtain anisotropic potentials[26] whose shape should be accurate near the equilibrium geometry, which is again linear inert gas–H-F. However, in this case, there were no data sensitive either to the absolute well depths of the potentials or to the potentials near the linear inert gas–F-H geometry. Subsequent measurements of the near-infrared spectra of these complexes by Fraser and Pine[192] suggest that the true well depths are 10–20 cm^{-1} deeper than those of ref 26. Fraser and Pine also demonstrated that the well depth is considerably greater for HF in its $v = 1$ state than for the vibrational ground state and have measured spectra involving the van der Waals bending vibration of Ar–HF in its $v = 1$ state. In addition, Lovejoy et al.[124] have measured infrared spectra corresponding to excitation of the overtone of the van der Waals stretching vibration in $v = 1$, which borrows intensity from the bending vibration by a Coriolis coupling mechanism. These new data should allow the determination of considerably improved potential energy surfaces for the inert gas–HF systems, especially if far-infrared spectra can also be measured. The inert gas–HF systems provide a particularly favorable case for investigating the dependence of intermolecular forces on the monomer vibrational coordinate.

The HF–HF system has also been extensively studied. Microwave and radiofrequency spectra have been measured[193,194] and have been used[195] to determine an intermolecular potential that should be accurate in the vicinity of the potential minimum. Very detailed high-resolution near-infrared spectra have also been observed,[125,196] and there have been several high-level ab initio calculations of the potential energy surface.[197]

The He–N_2 potential has also been extensively studied, using a wide variety of beam scattering, virial coefficient, and transport data. Keil, Slankas, and Kupperman[198] (KSK) proposed a potential based on total differential cross section measurements; this was found to be too weakly anisotropic to reproduce the rotational relaxation cross sections determined from SBE effects, and a modified version (KKM3) with an increased anisotropy was proposed.[199] Subsequently, Habitz, Tang, and Toennies[200] (HTT) proposed a semiempirical potential, while Fuchs et al.[71] developed two semiempirical potentials (HFD1 and HFD2); Faubel et al.[201] and McCourt et al.[202] tested all these potentials against measurements of total and state-to-state inelastic cross sections, virial coefficients, transport properties, and SBE cross sections and found that none of them was capable of reproducing all the experimental data. Banks et al.[101] performed CEPA calculations on He–N_2 and used the resulting potential for calculations of vibrational relaxation rates; their potential is considerably too shallow in the well region but is likely to be quite accurate at short range. Most recently, Candori et al.[203] have redetermined the isotropic part of the potential, and Gianturco et al.[204] have developed a full anisotropic potential (M3SV) that is considerably better than the earlier potentials, although significant discrepancies between experiment and theory remain.

The He–O_2 interaction has also been studied. Keil et al.[198] proposed a potential based on total differential cross section measurements, and Battaglia et al.[205] determined an isotropic potential from these measurements and from absolute and relative integral cross sections in the glory scattering regime. Faubel et al.[206] extended the latter study to include the anisotropy, on the basis of elastic and inelastic differential cross sections. The fine-structure spectrum of the He–O_2 van der Waals molecule has been predicted[207] but not measured.

There has also been a considerable amount of work on the interaction of heavier inert gases with N_2 and O_2. Pirani and Vecchiocattivi[208] have determined a potential for Ar–O_2 from a range of data, including high-energy integral cross sections, glory scattering, and (low-resolution) infrared spectroscopy. This potential, together with an earlier one due to Mingelgrin and Gordon,[209] has been used to predict the fine structure and radiofrequency Zeeman spectrum of the Ar–O_2 van der Waals molecule.[210] Candori et al.[211] subsequently modified the Ar–O_2 potential in the light of new differential cross section measurements and also determined an analogous potential for Ar–N_2. Mettes et al.[212] measured the Zeeman spectrum of Ar–O_2 and found that it was in somewhat better agreement with the modified potential of ref 211 than with the original one. McCourt et al.[213] have extended the semiempirical models[71] for He–N_2 to obtain potentials for Ne–N_2 and Ar–N_2 and have tested the resulting potentials against experimental second virial coefficients; all their potentials have substantially more anisotropy in the position of the repulsive wall than the empirical potentials. Ling et al.[214] have also developed semiempirical potentials for Ne–N_2 and have compared calculated second virial coefficients, viscosities, and diffusion coefficients with experimental values. They also investigated the effect of modifying the repulsive wall of the potential.

It may be noted that the He–N_2 and He–O_2 van der Waals complexes are dynamically quite different from those involving heavier inert gas atoms.[207] In the former, the anisotropy in the region of the potential minimum is comparable to or smaller than the monomer rotational spacings, so that the diatomic molecule executes nearly free rotation in the complex. For the heavier inert gases, the anisotropy is considerably larger, so that the monomer rotation is quite strongly hindered.

Interactions involving linear polyatomic molecules have also been investigated. Parker et al.[215] measured total differential cross sections (DCS) for He–CO_2, He–N_2O, and He–C_2N_2 and proposed anisotropic potential energy surfaces for these systems; the anisotropy of the potentials was determined from the damping of the diffraction oscillations in the DCS. For He–CO_2, they obtained additional information on the short-range part of the potential from second virial coefficients, viscosity and diffusion coefficients, and integral cross sections. Keil and Parker[216] subsequently extended the He–CO_2 study to include pressure-broadening cross sections and other transport properties. However, the resulting potential did not reproduce the differential energy loss spectra for rotationally inelastic He–CO_2 collisions measured by Buck et al.;[217] these authors suggested a modification of the repulsive anisotropy to bring the potential into agreement with their data. Danielson et al.[218] have recently remeasured the total DCS for He–CO_2 and obtained results consistent with the modified potential; they also made similar measurements for He–C_2H_2 and He–OCS and proposed potential energy surfaces for them.

The He–CO_2 van der Waals complex is insufficiently strongly bound to have been observed experimentally, but complexes of CO_2 with heavier inert gases have been observed.[219] Hough and Howard[220] have determined potential energy surfaces for Ar–CO_2 by least-squares fits to the microwave spectra; they also considered second virial coefficients and mean-square torque measurements. They obtained potentials that are quite well determined in the region of the equilibrium geometry (which is T-shaped), but rather uncertain elsewhere. The spectroscopic data appear to require a strongly anisotropic potential well, in order to reproduce the small zero-point bending amplitude in the ground vibrational state. However, this is in disagreement with the results of Rotzoll and Lübbert,[221] who concluded that Ar–CO_2 has a small well anisotropy on the basis of a lack of damping in the total DCS. By contrast, Buck et al.[222] interpreted their molecular beam differential energy loss spectra for Xe–CO_2 using a potential with a relatively large well depth anisotropy.

Pack et al. have determined anisotropic potentials for Ar–SF_6 and Kr–SF_6[223] and for He–SF_6 and Ne–SF_6[224] from multiproperty analyses considering second virial coefficients, viscosities, diffusion coefficients, and total DCS, Information on the aniostropy came mostly from the damping of oscillations in the DCS but is of rather different types for the different systems. For He–SF_6 it is the diffraction oscillations that dominate the DCS, and the damping of these contains information on the anisotropy in the position of the repulsive wall; conversely, for the heavier inert gases, the DCS are dominated by rainbow oscillations, and the damping of these contains information on the well depth anisotropy. For all the inert gas–SF_6 systems, the attractive potential is nearly isotropic, but the repulsive potential is weakest for approach of an inert gas atom along a threefold axis (between three F atoms), so that this is the equilibrium geometry.

Buck et al.[225] have determined an intermolecular potential for Ar–CH_4 from total DCS, and O'Loughlin et al.[226] have determined isotropic potentials for Ne–CH_4 and Ar–CH_4 from a combination of total DCS, viscosities, and second virial coefficients. Buck et al.[227,228] have measured differential energy loss spectra for Ar–CH_4 collisions and have used the results to determine semiempirical potentials for these systems. Once again, the equilibrium geometry is for approach of an inert gas atom over a threefold site.

In summary, complete potential energy surfaces have now been obtained for a variety of prototype systems, based both on spectra of van der Waals complexes and on scattering and bulk gas measurements, Most of the experimental observables are now well understood, and great advances have been made both in experimental techniques and in computational methods. We can now begin to understand the underlying trends that determine the potential energy surfaces and develop reliable methods for predicting intermolecular forces in systems that are not amenable to experiment.

IV. Hydrogen-Bonded Complexes

This section describes recent developments in the theory and calculation of the geometry, electrical properties, and potential energy surfaces of complexes in which hydrogen bonding is a possibility. Since 1983 there has been an explosion in the number of observations of these species and the ab initio literature has kept pace. It would be a thankless task to attempt a comprehensive list of all calculations, and our aim is rather a survey of the types of work being done, where possible pointing out a consensus on its physical interpretation. Some specific areas of controversy are also identified.

Experimental information on the structures and properties of hydrogen-bonded complexes is mainly obtained by microwave spectroscopy. Two methods have been used with great success for dimers in the ground vibrational state: Pulsed-nozzle, Fourier transform microwave spectroscopy[5,229] and molecular beam electric resonance spectroscopy (MBERS).[230,231] Both employ a collisionless molecular beam formed by expansion of the gas mixture and have consequent high sensitivity and resolution, allowing the detection of very weakly bound complexes. Both give spectra with detailed nuclear-quadrupole and nuclear spin–spin fine structure; MBERS can also measure components of the total dipole moment. These are valuable sources of information on electrical rearrangement and vibrational motion in the ground vibrational state of the complex. Conventional spectrometers can give complementary data on excited vibrational states of the more strongly bound complexes, though with poorer resolution.[5]

In this, as in any branch of science, experiment and theory are intimately connected. Sophisticated as the methods of measurement are, models and assumptions are still needed to extract average and equilibrium geometries, intermolecular stretching and bending force constants, and bond length and dipole moment changes from the raw spectra.[5] While the models can be tested for internal consistency, one task for theory is to check them against accurate calculation. Ab initio calculations can explore features of a complex and its potential surface with a detail inaccessible to experiment and, on occasion, have predicted results in advance of experiment. For example,[232] SCF calculations showed that $(HF)_2$ is bent and planar[233–235] with a nonlinear hydrogen bond[236] before the experimental determination of these features[237,238] and predicted the conformations of H_2O–HF and H_3N–HF[239] before they were observed.[240,241]

Perhaps more important than prediction is the explanatory role of theory. Many features of van der Waals complexes can be qualitatively and even semiquantitatively understood by using the theory of long-range intermolecular forces, where the properties of the complex are deduced from those of the isolated monomers. In particular, electrostatic models have been applied with some success to angular geometries,[242,243] induced dipole moments,[55,56] and bond length, vibrational frequency,[244] and polarizability changes[245] of hydrogen-bonded dimers. More rigorous approaches based on a long-range partition of the ab initio interaction energy include Morokuma analysis[28,45,246] and Stone's intermolecular perturbation theory (IMPT).[29,247] In these methods the total energy is partitioned into electrostatic, induction, dispersion, charge-transfer, and exchange-repulsion contributions. Doubts have been expressed about the validity of a long-range description in a region where overlap of monomer wave functions is nonnegligible,[248,249] but evidence is accumulating that long-range models mimic more accurate treatments of the interaction energy at separations from infinity down to the region of the van der Waals minimum.[45,49,48,118,250,251] These models are treated in section IVC.

Before giving a survey of calculations on specific complexes, we discuss some features of relevance to all such calculations. Most calculations on complexes use the supermolecule method in which the interaction energy is found by treating the whole complex as a single molecule, calculating its energy, and subtracting the energies of the monomers.

A. Structural Studies

A large number of weakly bound dimers have been studied by rotational spectroscopy; about 70 are listed in a recent review,[5] but the total is probably over 100. A useful bibliography of experimental structural studies is given by Novick in ref 252. Many of these have been studied in ab initio calculations of one kind or another.

One straightforward use of supermolecule calculations is to find the theoretical equilibrium geometry, either as a prediction or for comparison with experiment, and to calculate the corresponding dimerization energy. In a state-of-the-art calculation of this type the global minimum is found by optimizing the energy with respect to all geometric parameters, both inter- and intramolecular. Once a stationary point is found, it should be characterized as a minimum by examination of the eigenvalues of the second-derivative matrix. This is done most simply by analytic calculation of the vibrational frequencies: only points with $3N-6$ real frequencies (or $3N-5$ for a linear complex) are true minima.

Recent studies to this standard include work by Frisch, Pople, and Del Bene using the GAUSSIAN system of programs[253] to perform SCF and MP calculations on the dimers $(AH_n)_2$ formed from NH_3, H_2O, HF, PH_3, H_2S, and HCl[254] and the protonated species $(AH_n)_2H^+$.[255] The computed frequencies are useful in determining zero-point corrections to the dimerization energy. Strictly, the interaction energy should also be checked for BSSE by a counterpoise correction as in the SCF study of H_3N–HCN, $(HCN)_2$, HCN–HF, and H_2O–HF by Somasundram, Amos, and Handy.[256]

Using constrained geometry optimizations Sapse and Jain have found approximate equilibrium geometries by SCF or SCF/MP calculations for a series of heterodimers involving hydrocarbons C_2H_2, C_2H_4, C_2H_6, and C_6H_6 with HF[257] and with NH_3,[258] in broad agreement with experimental geometries where these are known. Ammonia is a strong proton acceptor but a weak proton donor; it is found to behave as a base even in forming hydrogen bonds to carbon in systems such as CF_3H–NH_3 (experiment,[259] predicted in early supermolecule work by Kollman et al.[260]). The strength of the interaction in these complexes was found to correlate with the charge on the hydrogen atom in the proton donor. Morokuma analysis of contributions to the interaction energy in C_2H_2/HF and C_2H_2/NH_3[261] showed that electrostatic forces determine the geometries of these complexes, a conclusion in agreement with the predictions of a simple model[243] described in the present paper.

Though it is sometimes safe to use chemical intuition to limit the range or symmetry of geometries searched, this can lead to incorrect results. Global minima may not in fact be the "likely" structures, as for the ammonia dimer (see later), or fine details such as the slight nonlinearity of a hydrogen bond may be missed. For some systems it would be difficult to guess the structure in advance, for example the "hydrogen-bonded" structure of B_2H_6–HF found by full optimization in a DZP basis by Rowlands and Somasundram[262] which has a lower symmetry than the average experimental structure[263] but is in qualitative agreement with it.

Ideally, though this is not always done, the results of a supermolecule calculation should be checked for convergence with respect to basis size. Calibration of basis sets as described in ref 264 is by no means an exact science, but some generalizations can be made. The basis must give an adequate description of the unperturbed electronic structure of the monomers and of properties that influence the interaction energy—the electrical moments and polarizabilities. Thus at least a doubly polarized double-ζ basis is required, with one (less diffuse) polarization set to describe nonspherical atomic densities (e.g., lone pairs) and a more diffuse set to describe monomer polarizability. Doubly polarized triple-ζ sets are routinely used for correlated calculations. Davidson and Feller[264] and Huzinaga[265] have reviewed the terminology and listed the various compilations of basis sets that are available. The accuracy of computed properties is thoroughly discussed by the van Duijneveldts[266] and Werner and Meyer.[76]

Some hydrogen-bonded systems for which variation of the calculated dimerization energy with basis set has been studied are $(H_2O)_2$,[109] $(NH_3)_2$,[267] $(HF)_2$,[110] and H_3N–HCl.[268] Use of very small basis sets can produce qualitatively incorrect results. For example,[268] minimal and split-valence sets predict that the ammonia–hydrogen chloride complex is an ion pair (H_4N^+–Cl^-), but addition of polarization functions to each basis gives a hydrogen-bonded structure (H_3N–HCl), in agreement with the latest experimental evidence.[269] Small basis sets were found to overestimate the interaction energy,[268] presumably because they give overlarge dipole and quadrupole moments.

Calculations that include electron correlation are of course more expensive than those using only SCF theory. Determinations of fully correlated potential surfaces for hydrogen-bonded complexes are correspondingly rare. One example is a calculation of the $(HF)_2$ surface by Michael, Dykstra, and Lisy.[270] Coupled cluster methods were used to find the optimum geometry in a triple-ζ singly polarized basis. Agreement with experiment at the 0.1% level was found for rotational constants, and HF stretching frequencies were predicted to within 1%.[270] A dipole moment surface was also calculated. For another complex, HCN–HF, Botschwina[271] has calculated harmonic and anharmonic stretching frequencies and frequency shifts including electron correlation by the CEPA (coupled electron pair approximation) method. His results are in good agreement with experimental data, though Amos et al.[272] suggest that the anharmonic stretch–bend interaction constants are nonnegligible.

A popular expedient for including some correlation is the use of Møller–Plesset (MP) perturbation theory,[273] also known as many-body perturbation theory

(MBPT). This technique takes the difference between the instantaneous interelectron repulsion and its Hartree–Fock average as the perturbation and can be carried to second, third, and higher order (MP2, MP3, ...) by a coupled Hartree–Fock approach. It is available as an option in several standard packages.[43,253] Some potential surfaces have been fully optimized at an MP level,[256,274–277] although often an equilibrium geometry is determined at the SCF level and correlation energy added for that single geometry.[254,255]

In the long-range description of intermolecular forces, intersystem correlation is the cause of the attractive dispersion force. Intersystem correlation, or dispersion, was found to have a significant effect on calculated bond lengths in $FH-NH_3$,[274] $FH-PH_3$,[275] $FH-OH_2$,[276] $FH-SH_2$,[277] and the corresponding HCl complexes. For example, MP2 correlation reduces the equilibrium intermolecular separation by 0.16 Å in $FH-PH_3$, 0.36 Å in $ClH-PH_3$,[275] and 0.15 Å in $ClH-NH_3$.[274] Another trend is found for the lengthening of the HX bond upon complex formation, $\Delta r(HX)$. In the doubly polarized basis sets used by Scheiner and co-workers the values of $\Delta r(HX)$ at the MP2 level are about double the SCF values. Thus on complexing to PH_3, the bond length of HF is predicted to increase by 0.0006 Å (SCF) or 0.012 Å (MP2). These results contradict those of van Duijneveldt et al.[278] in a smaller (split-valence) basis, from which it appeared that correlation had a minor effect on $\Delta r(HX)$. MP2 treatments can overestimate correlation effects in dipole moments by factors of up to two[37] and for similar reasons may exaggerate the influence of correlation on geometry.

An even less expensive way to include correlation effects in a potential surface is by adding dispersion terms, calculated as a multipole series, to the SCF surface. As discussed in section IID, the dispersion coefficients between monomers can be related to multipole polarizabilities at imaginary frequency for each monomer. Amos et al.[75] have calculated dispersion coefficients for the interaction of CO_2 and NH_3 by this method. They found the optimum geometry at the SCF level to be T-shaped with N coordinated to C, as in the experimental structure. The equilibrium orientation of the monomers is predominantly controlled by electrostatics[75] and is reproducible by the Buckingham–Fowler model;[242,243] taken with the agreement of SCF and experimental geometries, this suggests that the dispersion energy of this complex is a rather insensitive function of geometry. Although the SCF + dispersion treatment includes the effects of intermolecular correlation, it neglects the intramolecular component, which can modify the electrostatic and induction energies (through changes in moments and polarizabilities) and the short-range potential. In some calculations on a linear (i.e., nonequilibrium) structure of $(HF)_2$, Lischka[279] found a near-cancellation between inter- and intramolecular effects on the dissociation energy, length, and vibrational frequency of the van der Waals bond.

Some much larger hydrogen-bonded systems have been treated at a high level of theory. Examples that show what is possible are correlated calculations on the nitromethane dimer[280,281] and complexes of water and methanol with formamide.[282] The nitromethane dimer is of interest as a prototypical explosive system and in fourth-order MP calculations was found to have a cyclic C_{2h} equilibrium structure with two weak hydrogen bonds.[281] Only a very limited geometry optimization was possible for reasons of expense. Correlation contributes significantly to the interaction energy, changing the SCF value of −3.57 to −5.04 kcal mol^{-1}.[282] Formamide complexes are of obvious biological significance, and both water and methanol were found to form cyclic double-hydrogen-bonded structures in optimized CISD calculations[282] where the 1s cores on heavy atoms were replaced by pseudopotentials. Interaction energies of 9.5 and 8 kcal mol^{-1} were predicted for water and methanol complexes, respectively.

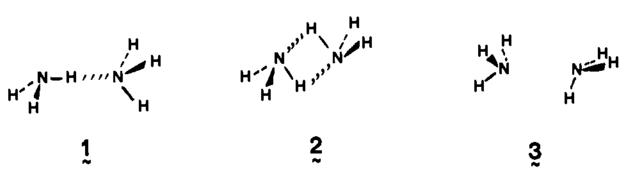


Figure 1.

At the opposite end of the scale of computer resources, Colwell et al.[283] have demonstrated the possibility of using microcomputers to make quantum chemical calculations. They calculated the equilibrium geometry for H_2S-HF in the 4-31G** basis using MICROMOL[284] (a smaller version of the CADPAC[43] program) running on a personal computer. With the wide availability of inexpensive computer power and the distribution of black-box program packages the trend toward "do-it-yourself" quantum chemistry is likely to continue.

Matrix Isolation Studies

We have discussed only complexes in the gas phase. A number of complexes have been studied in inert gas matrices by Fourier transform infrared spectroscopy (FTIR), notably by Andrews and co-workers.[285] These measurements complement those from gas-phase rotational spectroscopy in two ways. First, FTIR measures shifts in vibrational frequency induced by complex formation, though these are subject to large matrix-dependent effects. Second, by varying the conditions it is possible to observe secondary, less stable structures in addition to the thermodynamically favored product;[285] for example, both HCN–HF and the less stable HF–HCN are formed in solid Ar.

The large matrix effects make comparison with ab initio calculation tantalizingly inconclusive.[286,287] As ab initio treatment of a complex embedded in a large number of inert gas atoms is not feasible, a reliable model of the steric and electronic effects of the matrix would be very useful. Barnes has reviewed some simple models for matrix shifts.[288]

B. The Strange Case of the Ammonia Dimer

Perhaps the most interesting of the hydride dimers is $(NH_3)_2$. It is well established, both theoretically[110,289] and experimentally,[237,238] that in $(HF)_2$ and $(H_2O)_2$ the monomers are linked by a nearly linear hydrogen bond; a number of calculations have dealt with a similar structure 1 (Figure 1) for $(NH_3)_2$ (e.g., ref 267 and 290–293). Although 1 is generally predicted to be the global minimum, a local minimum has been found for a cyclic structure 2 of C_{2h} symmetry in some calculations.[294,295]

Recent experimental work by Klemperer and co-workers at Harvard[296,297] casts severe doubt on the validity of 1 as a structure for the gas-phase ammonia dimer. A nearly linear hydrogen-bonded structure is inconsistent with the measured spectroscopic constants for two vibrational states of $(NH_3)_2$ and one of $(ND_3)_2$. Most dramatically, the measured dipole moment of 0.75 D (component along the *a* inertial axis for $(NH_3)_2$) indicates substantial cancellation of the monomer dipole moments (each is 1.47 D). Though the experimental measurements cannot give unambiguous values for all the torsional angles, they are consistent with an average structure like 3.[297] In the absence of evidence for nonrigidity in the ground vibrational state of the complex,[297] it would appear therefore that the equilibrium structure is not 1. Furthermore, the fact that the complex has a nonzero dipole rules out the nonpolar 2. Klemperer et al. point out that even in the solid phase the hydrogen bonds between neighboring ammonia molecules are quite nonlinear (N–H–N angle of 164°) and argue that ammonia does not act as a proton donor in any known hydrogen-bonding interaction.[298]

How has ab initio calculation responded to the challenge posed by this new evidence? Much of the earlier work assumed a structure of the type 1 rather than performing a completely free optimization. Frisch, Pople, and Del Bene have studied the homodimers formed from a number of first- and second-row hydrides, including NH_3.[254] They optimized the geometries using 6-31G* and 6-31G^{+*} (doubly polarized) basis sets. At the stationary points the SCF energies were improved by adding p polarization functions on the hydrogens, and correlation energies were calculated by a variant of fourth-order MP perturbation theory. The SCF results show that $(NH_3)_2$ is indeed a difficult problem: in the smaller basis sets the cyclic structure 2 is the *global* minimum and 1 is only a transition state, while in the slightly larger basis 2 becomes a transition state and the C_s structure 1 becomes the global minimum! $(NH_3)_2$ is the only dimer studied in ref 254 for which such a switch of minima occurs.

When correlation and zero-point energies are taken into account, the best prediction of Frisch et al. is that the open C_s structure has a dimerization energy of 2.2 kcal mol^{-1} and that the C_{2h} structure lies only 0.2 kcal mol^{-1} above it (about 20% of the calculated barrier to conversion between equivalent minima in $(H_2O)_2$ and $(HF)_2$).[254] This remains true when the geometry is fully optimized at the MP2 level.[299] An experimental upper bound for the dissociation energy of $(NH_3)_2$ is 2.8 kcal mol^{-1}.[296]

Latajka and Scheiner[300] performed a detailed study of the potential energy surface for $(NH_3)_2$ using a small 4-31G* basis and, at selected points, a 6-31G** (1p,2d) basis (two sets of polarization functions on N and one on H) similar to the largest set used by Frisch et al. They found a global minimum in the SCF surface at the cyclic geometry and a transition state with near-linear hydrogen bonds 0.2 kcal mol^{-1} higher. BSSE was calculated but did not change this conclusion. Latajka and Scheiner find that the NH_3 dimer is extremely flexible, with a low-energy conversion path between linear and cyclic structures. The difference in stability between 1 and 2 is ascribed in their calculation to the difference in correlation energy. At the C_{2h} minimum the complex is nonpolar, in conflict with the observed dipole moment of 0.75 D. It is suggested in ref 300 that differences in zero-point energy along the cyclic–linear pathway lead to an average structure with the lower C_s symmetry, displaced by perhaps 10–15° from the cyclic equilibrium geometry. The same suggestion is made by Carnovale et al. in their study of the photoelectron spectroscopy of ammonia dimer.[301] Such a structure would have a dipole moment of about the right value. This might explain why isotopic substitution *lowers* the dipole moment,[297] but the explanation does not seem satisfactory; it is difficult to see how zero-point motion about a minimum can *lower* the average point group symmetry.

In summary, it is clear that the basis set limit for $(NH_3)_2$ has not yet been established, since small changes in basis can change the relative orientations and even the number of minima. A large-basis SCF + CI treatment of this complex would be of great interest, as would a detailed analysis of the electrostatic, induction, and dispersion contributions to the binding. Morokuma partition of a 4-31G calculation indicates that $(NH_3)_2$ is an "electrostatic" complex,[302] but results in this unpolarized basis may not be reliable. A study of the vibrational motion on the potential energy surface and its effect on the dipole moment would also be useful. On the experimental side, it would be interesting to know why there is no evidence of nonrigidity in the spectrum, when all the calculations point to a very flat surface in the region of interest—the flatness is of course the reason why it is so hard to pin down the minimum.

Liu et al.[303] suggest that large-amplitude motions do take place on the multiwell potential surface, but because of complicated torsional couplings do not give rise to vibrational splittings; they would therefore be "invisible" in the spectra measured by Klemperer and co-workers.[296,297] Liu et al. also find the dimer dipole moment, μ_a, to be a sensitive function of angle and, using an electrostatic model, find good agreement with the experimental dipole by reassigning one of the torsional angles from 60°[296,297] to 0°. Nelson and Klemperer[304] have made a detailed analysis of the tunneling–rotation levels of the dimer in the group of feasible permutation–inversion operations. They find that, even when tunneling is included as a feasible motion in the symmetry group, it is possible for the microwave spectrum to show no tunneling splitting.

Sagarik, Ahlrichs, and Brode[305] have obtained results that shed some light on the probable effect of electron correlation on the potential energy surface. They performed a partial optimization with polarized basis sets at the SCF level and introduced correlation by the CPF (coupled pair functional) method. The monomer geometries were frozen, and full characterization of the stationary points by calculation of the Hessian was not attempted. In their basis sets ([6s4p2d/3s1p] and [6s4p2d]) the SCF potential energy surface has a "linear" H-bonded minimum and the CPF surface has a minimum in a cyclic unsymmetric structure of the general type 3. Again the surface is very flat and the dipole very sensitive to geometry in the region of the minima. If the CPF minimum survives a full optimization, theoretical and experimental results may yet be in agreement for this troublesome case.

Ammonia dimer is clearly different in character from other dimers of fast-row hydrides. It also appears to differ from its second-row analogue $(PH_3)_2$. According to ref 254, $(PH_3)_2$ is bound by a tiny 0.3 kcal mol^{-1} arising from dispersion forces. With BSSE corrections the binding might well disappear altogether. In general, the second-row hydrides studied in ref 254 form only weak hydrogen bonds and have shallow, flat potential surfaces. For $(H_2S)_2$ this is confirmed by another study.[306] The second-row hydrides have smaller dipole moments than their first-row counterparts and separations are generally larger (because of larger van der Waals radii) so that on electrostatic grounds the weaker bonding is understandable. For example, in these calculations,[254] $(HF)_2$ is bound by 2.1 kcal mol^{-1}, whereas for $(HCl)_2$ the binding is only 0.9 kcal mol^{-1}. Protonated homodimers are also more strongly bound for first than second-row hydrides.[255]

C. Models for Structure and Properties

In a sense, a supermolecule calculation on a specific hydrogen-bonded complex is a model of that system, but as a picture of "the hydrogen bond" it is virtually useless without an interpretation in terms of broader chemical and physical concepts. In weakly bound complexes, the monomers retain to a large extent their separate identities; it is natural therefore to use the long-range theory of intermolecular forces to model the properties of the complex in terms of those of the isolated monomers.

Recent models for weakly bound complexes emphasize the importance of electrostatic forces and might be seen as a return to the early ideas of Pauling, Coulson, and others[307,308] on the hydrogen bond. The alternative charge-transfer viewpoint of Mulliken (see for example ref 309) is still used to rationalize known structures of complexes[249] but does not lead to a simple predictive scheme. The directional character, strength, and nature of the hydrogen bond in gas-phase dimers has been reviewed by Legon and Millen.[310]

Geometries

At the lowest level, a model for hydrogen-bonded complexes has to predict their overall shapes: which atoms are involved in the weak bond and what is the orientation of the monomer units. Morokuma-type decomposition of the SCF energy for a variety of hydrogen-bonded dimers,[45,48,250,262,302] has shown that the electrostatic contribution is a large fraction of the binding energy and, more importantly, dominates the angular variation of the total energy. The dispersion energy may contribute significantly to the binding energy but is usually a much slower function of the angular coordinates.

A basic model for geometries must therefore contain two ingredients: a representation of the electrostatic interaction to provide an angular minimum and a repulsive potential to hold the monomers apart. One such model is that of Buckingham and Fowler.[242,243] In it, the electrostatic interaction between monomers is calculated by using point multipoles on atoms and bond centers, and the repulsion is crudely modeled by hard spheres on heavy atoms. The multipoles are obtained from large SCF or SCF/MP calculations on the individual molecules, and the hard-sphere radii are taken from Pauling.[311] The geometry of a complex is predicted by finding a minimum in the electrostatic energy subject to the hard-sphere constraints.

Results of the model have been described[242] and many are tabulated in ref 243, so a correspondingly brief summary will be given here. For 30 or so hydrogen-bonded complexes the model gives structures in agreement with experiment; for example, it reproduces the linear H bonds in H_3N–HF, N_2–HF, and H_3P–HF, the nonlinear H bonds in $(HF)_2$, $(HCl)_2$, and H_2S–HF, and the H bonds to π systems in acetylene–HF and ethylene–HCl. Results for bond angles are often surprisingly accurate; for example, in H_2CO–HF, ∠COF is predicted to be 110°,[242] within 0.5° of the experimental angle.[312] The model has also been used to find likely starting points for ab initio optimizations: it finds the unusual B_2H_6/FH structure[262] and the T-shape for NH_3–CO_2.[75]

As noted earlier, the distributed multipoles are readily interpreted in terms of electronic-structure concepts such as lone and bonding pairs. This physical model is qualitatively compatible with an apparently "chemical" description such as that given by Legon and Millen.[313] Their empirical rule for hydrogen-bonded geometries states that HX attaches along the line of a nonbonded pair or, in the absence of a lone pair, perpendicular to the π cloud in a π-bonded system. The electrostatic model accounts for these observations but has the additional flexibility to allow for deviations from linearity and from idealized valence angles.[55]

The model is also economical. Departure from local spherical symmetry of the electron cloud around atoms is described by atomic dipoles and quadrupoles, where a single-site model would require central multipoles of high order. For example, the model used by Liu and Dykstra[59,244] for electrostatic and induction interactions in weakly bound complexes uses central octopole moments. The central multipoles of lowest order are often inadequate to explain the observed structures. For example, the dipole–dipole energy favors a linear geometry for HF–HF but the higher order central multipoles (implicit in the DMA description) produce the observed bent structure.[59] A bent geometry can also be predicted by point charges alone, if they are placed so as to simulate off-axis nonbonding pairs[45] or are fitted to reproduce central dipoles, quadrupoles, octopoles, and hexadecapoles.[47] Without attention to these features, point-charge models can give quite misleading electrostatic energies.[314,315]

Cases where a simple model fails are often as illuminating as those where it succeeds. The hard-sphere model tends to overemphasize the importance of hydrogen-bonded structures. For example, in ClF/HF with Pauling radii for Cl and F, the model predicts the hydrogen-bonded ClF–HF[243] rather than the experimentally observed "anti-hydrogen-bonded" HF–ClF.[316] A similar problem is found for HF–Cl_2. These difficulties can be traced to the crude form of the repulsive potential used in the model—the heavy-atom contact distances are too large for non-hydrogen-bonded geometries and so the electrostatic energy is underestimated. When the experimental separation is used, the model finds the correct angular geometry for both HF–ClF and HF–Cl_2.[243] Energy decomposition studies[48,250] of these and other "difficult" cases confirm that the angular geometry of the anti-hydrogen-bonded complexes is still controlled by electrostatics.

A further illustration is provided by the recently determined geometry of the SO_2/HCN complex.[317] Contrary to expectation, this molecule is "anti-hydrogen-bonded", HCN–SO_2. When Pauling radii are used, the model predicts a global minimum for a hydrogen-bonded structure SO_2–HCN and a shallower minimum for a S–N bonded structure. However, if the S–N separation used in the model is reduced, the secondary minimum deepens and eventually takes over as the global minimum for R(S–N) less than about 3 Å; the experimental value of this distance is 3 Å.[318] With this separation the angle between the figure axes of SO_2 and HCN predicted by the model is 80°, in excellent agreement with the measured value of 86°.[317,318]

Other treatments of the repulsive potential have been tried: Liu and Dykstra[59] use average radii estimated from known hydrogen-bonded complexes and include hard spheres for the H atoms: Price and Stone[315] use a smoothed penalty function to approximate hard spheres with radii taken from Pauling,[311] Brobjer and Murrell use the experimental center-of-mass to center-of-mass separation for calculations on $(HF)_2$,[47] and Amos et al.[319] use Lennard-Jones repulsion parameters. It may be possible to find *two* sets of heavy-atom radii, one appropriate to contacts X–H–Y and another to X–Y, to counter the tendency of the model to emphasize hydrogen-bonded structures.

Dykstra and co-workers[59,60,303] have used an electrostatics + induction model (with central multipoles and polarizabilities) to look at various complexes and clusters. They suggest that the complicated coupling of angular coordinates may introduce uncertainties into the analysis of the experimental structure for the ammonia dimer[303] and find that electrostatic predictions are in agreement with ab initio structures for the cyclic $(HF)_3$[59] and the T-shaped H_2–HF.[60]

Induced Dipole Moments

Large enhancements of dipole moment on formation of van der Waals complexes have been measured in some cases; for example, $\Delta\mu$ = 0.60 D for H_3P–HCN,[320] 0.60 D for OCO–HF,[321] and 0.49 D for OC–BF_3.[322] After allowing for zero-point effects the change in dipole is attributable to distortion of the monomer charge densities by induction, dispersion, and short-range forces. For complexes of polar monomers, where the electrostatic model of shape is useful, induction is likely to dominate the dipole.

A model for the induced dipole moment has been proposed.[55] It combines distributed multipoles describing the permanent charge cloud with distributed polarizabilities describing its response to an external field. Both are calculated ab initio using Stone's DMA[36] and DPA[54] methods. Predictions for several linear complexes are in spectacular agreement with experiment: e.g., for N_2–HCl, $\Delta\mu$ = 0.265 D (0.25 D);[323] for OC–HCl, $\Delta\mu$ = 0.381 D (0.39 D);[324] for OCO–HCl, $\Delta\mu$ = 0.441 D (0.45 D);[325] and for OCO–HF, $\Delta\mu$ = 0.617 D (0.60 D),[321] where the experimental values are given in parentheses. In these complexes there can be a substantial induced dipole on each partner; e.g., in OC–HCl the dipole enhancement consists of 0.245 D on OC and 0.136 D on HCl. Neglect of the latter contribution can give the false impression that large noninductive contributions are needed to explain the dipole.[324]

Dipole moments are also known for a number of other complexes,[312,322,326,327] including several involving BF_3. Novick[328] used a single-site inductive model for the dipole moments of Ar–BF_3, OC–BF_3, and N_2–BF_3 to estimate the quadrupole moment and polarizability of BF_3. Direct ab initio calculation shows these estimates to be rather poor[56] but this is a consequence of the inadequacy of a truncated single-site treatment. Fowler and Stone[56] used the DMA/DPA model to predict the dipole enhancements of these complexes, in excellent agreement with experiment, and concluded that they are indeed inductive in origin. A DMA/DPA treatment of the N_2O–HF complex gives indirect evidence that the permanent dipole moment of N_2O (of 0.16088 D)[329] is in the sense +NNO–. This sign is confirmed by a more recent experimental determination.[330]

Liu et al.[303] used a single-site model with high-order central moments and polarizabilities to predict a dipole moment surface for $(NH_3)_2$ in the region of the minimum.

An inductive model can also be constructed for the changes in polarizability caused by formation of a complex.[245] Dykstra, Liu, and Malik compared the predictions of their model for polarizability and hyperpolarizability with direct ab initio calculation for a range of geometries of the HF dimer and found agreement to within a few percent even at the equilibrium separation.[245] The coupled Hartree–Fock approach used necessarily excludes dispersion contributions to the polarizability properties, but the results are encouraging.

Changes in the nuclear quadrupole coupling constants have also been investigated.[331]

Bond Length Changes and Frequency Shifts

Although to a good approximation the monomer subunits in a complex B–HA retain their structures, they suffer small changes in geometry and shifts in vibrational frequencies. Legon and Millen[332] analyzed hyperfine coupling constants for a series of heterodimers B–HF and extracted values of Δr, the lengthening of the HF bond on complex formation, ranging from 0 to 0.016 Å (in CH_3CN–HF). The size of the effect correlates with the strength of the hydrogen bond.[332] Shifts in the HF stretching frequency have been measured for complexes in inert gas matrices[333,334] and in the gas phase.[335,336]

Such shifts are automatically included in the results from a full ab initio geometry optimization of the complex, as discussed in section IVA. However, it is clearly of interest to find a general model for geometric and vibrational shifts in terms of intermolecular forces. Experience with models for the geometry and dipole moment indicates that electrostatic and induction forces will account for much of the effect. The changes in structure and vibrational frequencies induced in a molecule by an external field are well-known.[337] The electrostatic energy of a molecule in a static field is

$$V^{\text{elec}} = -\mu_\alpha F_\alpha - \tfrac{1}{3}\Theta_{\alpha\beta}F_{\alpha\beta} - \ldots \qquad (40)$$

and each permanent moment is a function of the geometry of the molecule (i.e., a property surface), so that V^{elec} constitutes a field-dependent addition to the vibrational potential energy surface. For simplicity, consider a diatomic molecule. The field-free potential energy is

$$U(r) = \tfrac{1}{2}f_{rr}(\delta r)^2 + \tfrac{1}{6}f_{rrr}(\delta r)^3 + \ldots \tag{41}$$

and the moments are

$$\mu_z(r) = \mu_z{}^{\mathrm{e}} + \mu_z'(\delta r) + \tfrac{1}{2}\mu_z''(\delta r)^2 + \ldots \tag{42}$$

$$\Theta_{zz}(r) = \Theta_{zz}{}^{\mathrm{e}} + \Theta_{zz}'(\delta r) + \tfrac{1}{2}\Theta_{zz}''(\delta r)^2 + \ldots \tag{43}$$

where δr is the departure from the equilibrium bond length and $\mu_z{}^{\mathrm{e}}$ and $\Theta_{zz}{}^{\mathrm{e}}$ are the dipole and quadrupole moments for the equilibrium geometry. In the field, the molecule relaxes to a new bond length and the shift is found by differentiating $U(r) + V^{\mathrm{elec}}$. It is

$$\Delta r = (\mu_z'/f_{rr})F_z + \tfrac{1}{2}(\Theta_{zz}'/f_{rr})F_{zz} + \ldots \tag{44}$$

and the force constant changes by

$$\Delta f_{rr} = \left(\frac{f_{rrr}\mu_z'}{f_{rr}} - \mu_z''\right)F_z + \tfrac{1}{2}\left(\frac{f_{rrr}\Theta_{zz}'}{f_{rr}} - \Theta_{zz}''\right)F_{zz} + \ldots \tag{45}$$

Higher terms arise from the induction energy and from higher derivatives of the field. These equations also neglect the effect of short-range forces, and this may not be warranted.

Liu and Dykstra[244] have applied this theory to van der Waals complexes of HF, where the fields $F_\alpha, F_{\alpha\beta}, \ldots$ arise from the permanent and induced moments of the neighboring molecule. They use central multipoles (up to hexadecapole), polarizabilities, and hyperpolarizabilities. Vibrational frequency shifts are calculated very well by a model that includes induced moments (agreeing with experiment to within a few percent in all but one case), but not so well by the electrostatic model alone. Comparison of the results for bond length shifts[244] with those derived from experimental quantities[332] shows the same quality of agreement, with a suggestion that the model tends slightly to overestimate the effect.

In other applications, we have seen that a distributed model improves predictive power. A simple distributed model can be constructed for bond length and frequency shifts as follows. The total molecular multipole moments can be recovered from a DMA[36,37] as sums of site contributions

$$q^{\mathrm{A}} = \sum_{\mathrm{a}\in\mathrm{A}} q^{\mathrm{a}} = \sum_{\mathrm{a}\in\mathrm{A}} \tilde{q}^{\mathrm{a}} \tag{46}$$

$$\mu_\alpha{}^{\mathrm{A}} = \sum_{\mathrm{a}\in\mathrm{A}} [\mu_\alpha{}^{\mathrm{a}} + q^{\mathrm{a}}R_\alpha{}^{\mathrm{a}}] = \sum_{\mathrm{a}\in\mathrm{A}} \tilde{\mu}_\alpha{}^{\mathrm{a}} \tag{47}$$

$$\begin{aligned}\Theta_{\alpha\beta}{}^{\mathrm{A}} = \sum_{\mathrm{a}\in\mathrm{A}}\Bigg[\Theta_{\alpha\beta}{}^{\mathrm{a}} + \bigg(\frac{3}{2}\mu_\alpha{}^{\mathrm{a}}R_\beta{}^{\mathrm{a}} + \frac{3}{2}\mu_\beta{}^{\mathrm{a}}R_\alpha{}^{\mathrm{a}} - {}\\ \mu_\gamma{}^{\mathrm{a}}R_\gamma{}^{\mathrm{a}}\delta_{\alpha\beta}\bigg) + \frac{1}{2}q^{\mathrm{a}}(3R_\alpha{}^{\mathrm{a}}R_\beta{}^{\mathrm{a}} - (R_\gamma{}^{\mathrm{a}})^2\delta_{\alpha\beta})\Bigg] = \sum_{\mathrm{a}\in\mathrm{A}} \tilde{\Theta}_{\alpha\beta}{}^{\mathrm{a}}\end{aligned} \tag{48}$$

where q^{a}, μ^{a}, and Θ^{a} are point multipoles on site a at position R^{a} in molecule A, and the tilde denotes the total contribution from all point multipoles on site a to the molecular multipole of molecule A. The total electrostatic energy of molecule A in the field of molecule B is

$$V^{\mathrm{elec}} = \sum_{\mathrm{a}\in\mathrm{A}} [q^{\mathrm{a}}\Phi^{(\mathrm{a,B})} - \mu_\alpha{}^{\mathrm{a}}F_\alpha{}^{(\mathrm{a,B})} - \tfrac{1}{3}\Theta_{\alpha\beta}{}^{\mathrm{a}}F_{\alpha\beta}{}^{(\mathrm{a,B})} - \ldots] \tag{49}$$

where Φ is the electrostatic potential and the superscript (a,B) denotes a potential or field at *site* a arising from the charge distribution of *molecule* B. In calculating the derivative of V^{elec} with respect to bond length for a diatomic molecule, one must remember that both the moments and the electrostatic potentials are functions of δr. As the diatomic molecule stretches, the site multipoles change, but the site is also moving to a different position in the field. The result is

$$\Delta r \approx \left[\left(\frac{\partial V^{\mathrm{elec}}}{\partial r}\right)\Big/ f_{rr}\right] \tag{50}$$

$$\begin{aligned}\Delta r = \sum_{\mathrm{a}\in\mathrm{A}}\Bigg[\left(\frac{\partial\tilde{q}^{\mathrm{a}}}{\partial r}\right)\Phi^{(\mathrm{a,B})}/f_{rr} - \left(\frac{\partial\tilde{\mu}_\alpha{}^{\mathrm{a}}}{\partial r}\right)F_\alpha{}^{(\mathrm{a,B})}/f_{rr} - {}\\ \frac{1}{3}\left(\frac{\partial\tilde{\Theta}_{\alpha\beta}{}^{\mathrm{a}}}{\partial r}\right)F_{\alpha\beta}{}^{(\mathrm{a,B})}/f_{rr} - \ldots\Bigg]\end{aligned} \tag{51}$$

and for the force constant shift

$$\begin{aligned}\Delta f_{rr} = \sum_{\mathrm{a}\in\mathrm{A}}\Bigg\{\Bigg[\frac{f_{rrr}}{f_{rr}}\left(\frac{\partial\tilde{q}^{\mathrm{a}}}{\partial r}\right) - {}\\ \left(\frac{\partial^2\tilde{q}^{\mathrm{a}}}{\partial r^2}\right)\Bigg]\Phi^{(\mathrm{a,B})} - \Bigg[\frac{f_{rrr}}{f_{rr}}\left(\frac{\partial\tilde{\mu}_\alpha{}^{\mathrm{a}}}{\partial r}\right) - \left(\frac{\partial^2\tilde{\mu}_\alpha{}^{\mathrm{a}}}{\partial r^2}\right)\Bigg]F_\alpha{}^{(\mathrm{a,B})} - {}\\ \frac{1}{3}\Bigg[\frac{f_{rrr}}{f_{rr}}\left(\frac{\partial\tilde{\Theta}_{\alpha\beta}{}^{\mathrm{a}}}{\partial r}\right) - \left(\frac{\partial^2\tilde{\Theta}_{\alpha\beta}{}^{\mathrm{a}}}{\partial r^2}\right)\Bigg]F_{\alpha\beta}{}^{(\mathrm{a,B})} - \ldots\Bigg\}\end{aligned} \tag{52}$$

The potential and field of molecule B can be evaluated from the permanent site multipoles in B, and derivatives of the site multipoles can be calculated by a coupled Hartree–Fock scheme or by finite differences. If necessary, the effects of induction could be included by using DPA site polarizabilities. Calculations using this model will be reported in a later publication.

Other properties that may be amenable to modeling are the electric field gradients at nuclei (accessible from experiment via nuclear quadrupole splittings) and the dipole and polarizability derivatives (governing intensities of infrared and Raman transitions).

Some ab initio studies on electric field gradients in the N_2–HF complex have been performed by Cummins et al.[338] and Benzel and Dykstra.[339] The calculations successfully predict the trend in going from free N_2 to the complex, but a quantitative comparison is made difficult by the need for vibrational averaging, for which harmonic wave functions may be inadequate.[338] In calculations on clusters $(H_2O)_n$ (n = 2–5)[340] and $(NH_3)_n$ (n = 2–7),[251] it is found that most of the change in electric field gradient between the gas phase and the condensed phase (simulated by a cluster) can be accounted for by an electrostatic model.[251]

Accuracy of calculated dipole derivatives is crucially dependent on the quality of the basis set,[341] and it is notoriously difficult to extract these derivatives reliably from experiment. These remarks apply with added force to the polarizability derivatives. In addition, it appears that intramolecular polarizability derivatives are subject to large secondary BSSE effects,[342] much more so than the corresponding dipole derivatives. Some attempts to construct long-range models of these quantities have been made[251,343] but it seems that such models fail because they are unable to describe the changes caused by an atom moving in a bonding environment.[251]

D. Complexes of Aromatic Molecules

Electrostatic models are not expected to be adequate for all complexes of polar and quadrupolar molecules. In some cases, such as OCO–HF, the experimental structure is the outcome of a delicate balance of contributions.[48] In others, the dispersion energy may be significantly anisotropic. One interesting class of complexes where this may be true is the homo- and heterodimers of aromatic molecules, for which the interpretation of the experimental evidence is not totally clear and different models can give conflicting results.

The Buckingham–Fowler model[242,243] has been used by Price and Stone[344] to predict geometries for complexes of *s*-tetrazine with HCl, H_2O, C_2H_2, benzene, and *s*-tetrazine, and of benzene with C_2H_2, benzene, anthracene, and perylene. For the larger complexes, the model predicts a number of distinct local minima, closely spaced in energy. There is some experimental evidence of geometrical isomerism in aromatic complexes; for example, Haynam et al.[345] assign laser-induced-fluorescence spectra of *s*-tetrazine dimer to two isomers, one with parallel rings and one T-shaped. In the cases where the structure of a complex is experimentally well determined, it usually corresponds qualitatively to one of the minima predicted by the model.[344] Price and Stone conclude that the electrostatic energy plays a major role in determining these structures, though it is less dominant for aromatic complexes than for those of small polar and quadrupolar molecules, because the dispersion energy is much more anisotropic. Even in a model that includes dispersion it is important to have a good representation of the electrostatic effects of the π clouds, such as that provided by a DMA. Price and Stone demonstrate the inadequacy of previous point-charge models in this respect.

To realize, however, that we have much to learn about aromatic dimers, consider the simplest case of all, the benzene dimer. In molecular beam electric deflection experiments, it was found that $(C_6H_6)_2$ is polar[346] and an asymmetric rotor,[347] A T-shaped structure was proposed, in agreement with the nearest-neighbor orientation in the solid and with the long-range quadrupole–quadrupole interaction. However, recent spectroscopic data appear to require that the two monomers be equivalent; a slipped-parallel C_{2h} structure[348] and a C_{2v} V-shape[349] structure have been proposed by different groups. The electrostatic energy does not decide between the various minima,[344] and it is not obvious which one of them will be favored by the dispersion interaction.

Some ab initio supermolecule calculations on aromatics have been performed by Pawliszyn et al.[350] on the homo- and heterodimers of benzene and *s*-tetrazine. SCF energies were found for various coplanar and perpendicular geometries, using the minimal STO-3G basis. Dispersion effects were added as an atom–atom R^{-6} potential, parameterized from ab initio calculations on azabenzenes.[351] The T-shaped benzene dimer was the most stable of the arrangements considered, though since these did not include any V-shaped or slipped-parallel configurations, the results are not conclusive. Since minimal basis sets also tend to give poor multipole moments, it is probable that the modeling approach using a DMA from a high-quality monomer wave function is more reliable than the rather limited supermolecule results. Modeling is certainly less expansive and allows a more extensive search of the potential energy surface for "unexpected" structures.

Amos et al.[319] use a simple (repulsion + electrostatics + dispersion) model to find equilibrium structures for various perylene complexes, in order to interpret solvent shifts in the laser-induced fluorescence of perylene. For 1:1 complexes the solvent molecule (e.g., benzene) is predicted to lie over the central perylene ring. Stone and Price[344] show that a point-charge model of the electrostatic energy, as used in ref 319 and 352, can lead to a spurious minimum for central binding. A more complete treatment of the electrostatics suggests binding of the benzene to the periphery of the perylene molecule. It is not clear whether such geometries would be compatible with the observed red shifts. The Nottingham group[353] is now investigating the effects of changes in the electrostatic component of their model on the predicted results.

In summary, the complexes of aromatic molecules are not yet fully understood from either an experimental or a theoretical viewpoint. These complexes are severe tests of simple models and ab initio computation alike and are likely to remain a challenge for theoreticians for some time to come. When a scheme for calculating distributed dispersion coefficients from ab initio wave functions becomes available, aromatic complexes will be among the first targets for modeling.

V. Conclusions

Much progress has been made toward an understanding of the structure and properties of van der Waals molecules. The basic theory of intermolecular forces is well developed, and much is known about the best way to parameterize intermolecular potentials. Direct ab initio calculations are not yet capable of calculating intermolecular potentials except for the smallest systems, but methods that partition the intermolecular potential into contributions from repulsive, electrostatic, induction, and dispersion forces are very promising. For larger molecules, single-center expansions of the attractive forces are not adequate, and distributed models for multipole moments and polarizabilities are important. Complete potential energy surfaces have been developed for a range of prototype atom–diatom and diatom–diatom systems, using a combination of theoretical calculations and high-quality experimental data.

For complexes involving larger monomers, the information available is less complete. The geometries of strongly bound complexes are now well understood, in that they can be reproduced satisfactorily by accurate calculations and explained by simple physical models. However, the dynamics of the motion on the potential energy surface remain to be elucidated; simple harmonic models are not entirely adequate. For weaker complexes where dispersion is more important, such as those of aromatic molecules, theory and experiment have yet to produce satisfactory accounts of the equilibrium geometry, although some of the factors involved have been identified.

The weakness of the bonding and the large-amplitude vibrational motion mean that some of the accepted concepts that we apply to "chemically bound" molecules need to be modified; for example, properties may vary substantially on siotopic substitution and on vibrational, or even rotational, excitation. However, the weakness of the interaction also allows us to consider a van der Waals molecule A–B as a pair of molecules A and B: our knowledge of the properties of the free molecules A and B then gives us the basis for a description of the complex.

From a detailed understanding of the interactions in van der Waals molecules, we can proceed to more complicated systems that are of interest in physics, chemistry, and biology; these include surface interactions, condensed phases (including solutions, liquids and solids), micelles, polymers, biomacromolecules, and membranes. In particular, the distributed models of attractive forces developed from studies of van der Waals molecules will make it possible to go beyond the site–site potentials and point-charge models that are commonly used in modeling molecular interactions in biological systems.[354]

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