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Current Themes in Microwave and Infrared Spectroscopy of Weakly Bound Complexes

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I. Introduction

High-resolution spectroscopy of weakly bound molecular complexes held as one of its earliest goals the detailed understanding of the interactions between molecules. The prospect of connecting a molecular-level description of small clusters with a more familiar understanding of bulk materials has also been a pervasive driving force. Out of these ideas has grown a body of science which encompasses a surprisingly rich variety of topics, and the volume of information now available about weakly bound systems has become truly staggering. The goal of this article is to illuminate some of the recent trends which continue to drive further work in this area. In part *II* we discuss recent studies on a number of important weakly bound dimers, focusing both on their internal dynamics and on the dependence of the interactions on monomer vibrational excitation. Section III addresses the progress and implications of high resolution studies of larger clusters, and in section IV, we summarize the status of predictive methods (both electrostatic modeling and *ab initio* theory). Finally, in section V, we review a number of recent applications to the study of systems which lie "on the brink of chemistry" and which thus offer the hope of bridging the study of "nonchemical" interactions with the more familiar understanding of truly chemical phenomena.

We limit the scope of this article to results derived primarily from high-resolution infrared and microwave spectroscopy. In doing so, a conspicuous omission is the spectroscopy and photophysics of optically excited van der Waals molecules, and, in particular, the almost explosive progress which has occurred in recent years in the optical spectroscopy of open shell species. Fortunately, several excellent reviews on the latter have recently appeared.[1] Numerous other reviews covering a broad range of topics are available as well,[2–25] and an extensive bibliography of references has been compiled.[26]

II. Recent Studies of Dimers

The earliest high-resolution studies of weakly bound dimers focused on structures of the complexes and on zero point motions of the monomer units in

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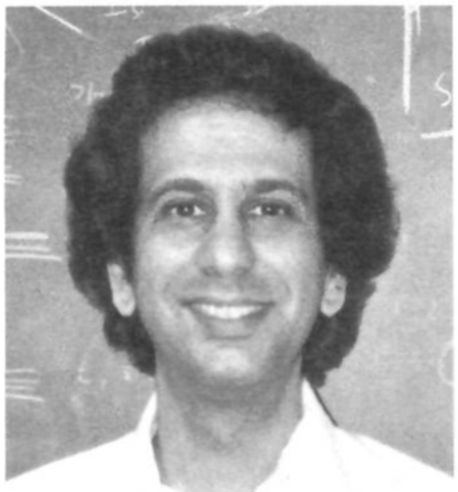
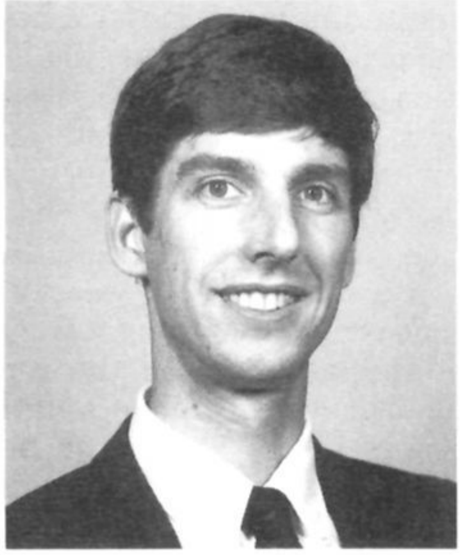


Kenneth R. Leopold received his B.S. degree in Chemistry from the State University of New York at Stony Brook in 1977, and his Ph.D. in Chemistry from Harvard in 1983, working with William Klemperer. Following a postdoctoral fellowship in K. M. Evenson's laboratory in Boulder CO, he joined the faculty at the University of Minnesota in 1986 where he is currently Associate Professor of Chemistry. His interest are in the spectroscopic investigation of weakly bound and partially bound systems.



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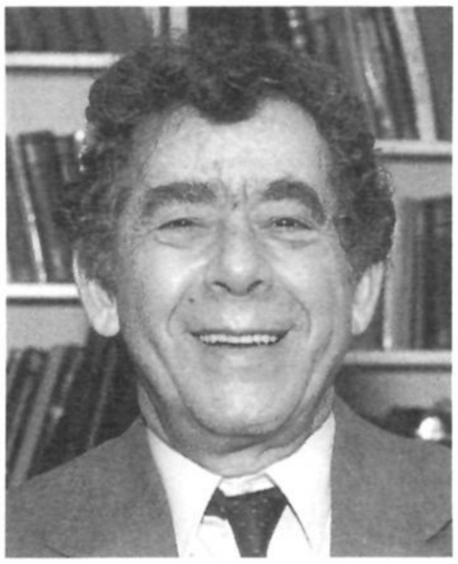
the region of the potential energy minimum. Not only did these features provide the most basic characterization of a complex, but they were, quite fortunately, the ones which were most readily available from microwave techniques used at the time. Since these early studies, however, significant advances in experimental and theoretical methodologies have made possible the observation and interpretation of spectra at much higher energies. As a result, with a myriad of structures already accurately known, much of the emphasis has shifted toward a more global understanding of the intermolecular potential surfaces and to a clearer description of the internal dynamics which occurs on them. In a parallel vein, the vibrational dependence of the interactions has also become a significant issue, due to the crucial role played by monomer-localized infrared spectra. The topics highlighted in this section reflect these trends. Also included, however, is some recent work on the most fundamental, but previously inaccessible systems (the rare gas dimers), which revives some the spirit of simplicity enjoyed by the earliest studies of weakly bound complexes.

Professor Steward E. Novick (1945) studied chemistry at the State University of New York at Stony Brook (B.S. 1967) where he got his first taste of research as an undergraduate in the laboratory of Professor Theodore Goldfarb and at Brookhaven National Laboratory. He went on to Harvard University (Ph.D. 1973) to work in the molecular beams laboratory of Professor William Klemperer where he was fortunate enough to be in the right place at the right time in order to participate in the very beginnings of the high-resolution microwave studies of weakly bound complexes produced in supersonic jet. After a postdoctoral stint with Klemperer, he then went on to a research associateship with Professor W. Carl Lineberger at the Joint Institute of Laboratory Astrophysics in Boulder, CO, where he worked on photodetachment and photoelectron spectroscopy of negative ions. In 1978 he joined the Chemistry Department of Wesleyan University where he is currently Professor of Chemistry. During a sabbatical semester at the National Institute for Standards and Technology in 1987 he learned the technique of pulsed jet Fourier transform microwave spectroscopy, a technique which has been transported to his own laboratory at Wesleyan in aid of his major research interests in the elucidation of the structure, bonding and dynamics of weakly bound complexes and in the structure, bonding and electronics of radicals. He is the author of 40 scientific papers and he is a founding member of the Southern New England Microwave Consortium.



William Klemperer is a Professor of Chemistry at Harvard University. He joined the faculty in 1954 as instructor after completing his Ph.D. with George Pimentel at Berkeley. From 1979 to 1981 he was Assistant Director of the National Science Foundation (for Mathematical and Physical Sciences). His research interests are in chemical physics. He has taught analytical and inorganic chemistry as well as his major area of physical chemistry.

A. Angular–Radial Coupling in Rod–Ball Systems

The interaction of the inert gases with the hydrogen halides has been studied extensively, and these simple rod–ball systems have a seemingly natural extension in the rare gas complexes with HCN.

Indeed, the dipole moment of HCN is only 2–3 times larger than that of HF and HCl, and it might, therefore, be expected that close similarities between the Rg–HX and Rg–HCN structures would exist. From the very first observation of Kr–HCN,[27] however, it was apparent that this was not the case. To date, the most extensively studied member of the Rg–HCN series is Ar–HCN,[28–37a] and there is a quite good picture, today, of the nature of the potential energy surface and of the internal dynamics which occur on it. The large amount of data now available has made clear that strong angular radial coupling, together with tunneling outside the classical turning point of the bending potential, is at the root of a variety of spectroscopic anomalies which distinguish this system from the ordinary. In its interaction with the inert gases, HCN (and indeed also the isoelectronic HCCH discussed below) are best pictured as modestly extended rods, in contrast to the hydrogen halides which appear to be slightly distorted spheres. As a consequence, the dynamics of the Rg–HX systems allows the angular and radial motions to be at least approximately separated, while for Ar–HCN, the angular–radial coupling becomes significant. In Ar–HF, for example, the rotational constants of all angular excited states are within 1% of that of the ground state, while for Ar–HCN the rotational constants of the angular excited states differ by as much as 25% from that of ground state.[37a] Interestingly, these effects were understood theoretically[32,34] before experiments.

The lowest frequency bending vibrations of Ar–HCN are a Σ state at 5.500 164 7(4) cm^{-1} and a Π state at 6.070 346 6(2) cm^{-1}.[37] The $J = 1$ level of free HCN is at 3 cm^{-1}, showing that the potential hindering rotation (and concomitant radial contraction) is exceptionally feeble. It is noteworthy that in the first excited CH valence stretching state of HCN, the equivalent Π bending state[31,33] is at 8.057 95(17) cm^{-1}. This dramatic change of 30% in frequency illustrates the possible sensitivity of very low frequency vibrations to other coordinates.

Ne–HCN has also been well-characterized by its rotational spectrum.[38] The magnitude of the centrifugal distortion is a factor of 10 greater than that in Ar–HCN,[28] showing undoubtedly the effects of large angular–radial coupling. The surprisingly large HCN/DCN isotope effect upon the ground state centrifugal distortion which is observed for Ar–HCN, however, is not seen. This indicates that tunneling into the 90° T-shaped configuration is irrelevant in Ne–HCN as a consequence of the much larger angular excursion that exists within the classical turning point of the effective bending potential. Indeed for Ne–HCN, $\langle``\theta"\rangle = \cos^{-1}\{[(2P_2(\cos\theta) + 1)/3]^{1/2}\}$ is 46°, indicating a broader angular distribution than that which exists in Ar–HCN (31°). For Kr–HCN, on the other hand, the observed centrifugal distortion is about one-fourth that of Ar–HCN but shows identical isotopic dependence. Several transitions of He–HCN[39] have also been observed, but the data are too preliminary to incorporate in the present discussion.

There remains one exceptional puzzle in the Ar–HCN problem. A doublet rotational transition, $J = 1–2$, $K = 1$ with B within 1% of the ground state has been observed.[36] Since the ground state of Ar–HCN is linear and the excited Π state well characterized, it appears likely to us that this transition is of an Ar–HCN complex with valence vibrational degeneracy in the HCN submolecule. The ν_2 vibration of HCN is poorly cooled in expansions with inert gases and therefore has high population in the jet. This assignment implies a long (~1 ms) predissociative lifetime for the state. It is noteworthy that this type of state is also observed in Ne–HCN.[38]

Rare gas complexes of HCCH (which is isoelectronic with HCN) have also been studied. The dipole moment of Ar–HCCH is small, 8.966(10) × 10^{-32} Cm (0.026 97(3) D), but there have nonetheless been successful studies of its rotational spectrum,[40,41] and the complex is seen to have a T-shaped minimum energy configuration. As with Ar–HCN, the angular rigidity is quite weak, and thus interpretation of the rotational and rotation–vibration spectra prove to be quite complex.[42,43] As might be expected, however, the centrifugal distortion does not appear pathologically large, indicating that angular–radial coupling is less pronounced for a rod–ball system with a T-shaped equilibrium geometry than it is for the linear shape. The dynamics of the He–HCCH system has been treated,[44] and the system is quite nonrigid, giving a very complex rotation–vibration spectrum near 3000 cm^{-1}.[45]

B. Some Questions about Rod–Ball Systems

Of considerable interest is the nature of the intermolecular potential of the rod–ball system in general. In particular, the question may be asked as to whether there are numerous local pockets on the rod in which the ball may rest. This problem has arisen in the Ar–HCCH system where a combination of semiempirical modeling, Hartree–Fock plus distributed atom–atom damped dispersion, and the fitting of the rotation–low frequency vibration spectra has led to the conclusion of a double-minimum potential.[46] This point appears important to test further since the question of accuracy of Hartree–Fock plus atom–atom interaction is important. We note that early modeling of the potential energy surface of Ar–HCN by a similar method predicted bent equilibrium geometries[29] and was shown to give a poor representation of the low frequency vibrational levels.[35]

More generally, the existence of isomers of rod–ball type inert gas–molecule binary complexes has not yet been widely established.[47] Although the potential energy surfaces for Ar–HF and Ar–HCl, for example, show minima at $\theta = 0°$ and 180°, the state with highest probability density at 180°, the Σ bending state (v100), shows no evidence of being metastable, and has large probability amplitude for $\theta < \pi/2$.

The inert gas–halogen species are perhaps more likely systems in which to find both linear and T-shaped isomers. Ar–ClF[48] and Kr–ClF,[49] for instance, have linear equilibrium geometries, as determined by rotational spectroscopy, while for a number of halogen complexes, T-shaped structures have been established by rotational analysis of electronic transitions. The electronic spectrum of

Ar$-I_2$ has been carefully examined in the B$-$X system,[50,51] and it has been suggested that both isomers do, in fact, exist simultaneously.[52] It has been further suggested that the latter is the carrier of the sharp bands in the B$-$X system, while the former has a continuous spectrum readily observable by laser induced fluorescence. Indeed, the linear isomer has been implicated in the "one atom cage effect"[51] seen in the photodissociation dynamics of the complex. For Ar$-Cl_2$, an electron structure calculation suggests that the two isomers are virtually isoenergetic.[53] The existence of the T-shaped form has recently been established by rotational spectroscopy.[54]

C. Tunneling Dynamics in Homogenous Dimers

Homogenous dimers have played a central role in the theory of intermolecular forces due to their close connection to the properties of one-component systems (e.g. crystal structures, boiling points, vapor pressure curves, and transport properties of pure gases). In many of the homogenous dimers the two bonding partners occupy structurally inequivalent sights giving rise to an interesting tunneling motion which allows the subunits to interchange bonding roles in the complex. First observed and extensively characterized in $(HF)_2$,[55-80] interchange tunneling has been studied in a number of systems, including $(SO_2)_2$,[81] $(HCl)_2$,[82-90] $(NH_3)_2$,[91-99] $(H_2O)_2$,[20,94,100-119] $(HCCH)_2$,[77,120-126] $(H_2CO)_2$,[127] and $(C_6H_6)_2$.[128] The observed splittings range from 70(1) kHz in $(SO_2)_2$[81] to more than 10 cm^{-1} in $(HCl)_2$[87,90] and $(NH_3)_2$.[98] In each case the tunneling motion can be pictured as a hindered, geared internal rotational motion of the two subunits about their centers of mass. Several examples are illustrated in Figure 1. The potentials have two minima in $(HF)_2$ and $(HCl)_2$, four minima in $(HCCH)_2$, and eight minima in $(H_2O)_2$. In addition to the interchange tunneling, a number of the homogenous dimers, such as $(H_2O)_2$ and $(NH_3)_2$, exhibit additional tunneling processes which further complicate the energy-level splitting patterns. The analysis of these complex spectra have been greatly facilitated by the molecular symmetry group of Longuet-Higgins,[129] which was first applied to dimers by Dyke and co-workers[56,100] in studies of $(HF)_2$ and $(H_2O)_2$.

The rich tunneling dynamics possible in the homogenous dimers is illustrated by the case of $(H_2O)_2$. As shown in Figure 2, hydrogen interchange tunneling splits each C_s symmetry rigid rotor energy level into six tunneling sublevels.[100] The largest tunneling splitting, as initially inferred[105] from a semiempirical potential energy surface,[130] is also pictured in Figure 2 and results from an interchange of the two protons on the proton acceptor$-$water unit. The next most important tunneling process is the acceptor$-$donor interchange motion,[105] which allows the two subunits to exchange bonding roles in the complex. A third motion allows for interchange of the proton donor hydrogens and is thought to go through a bifurcated transition state.[105,114] Extensive isotopic studies of 10 of the 11 possible deuterated complexes,[101,110,112,116-119,131-134] together with one-dimensional modeling of the tunneling dynamics[119] and *ab initio* calculations of the various tunneling barriers,[114] have been undertaken to unravel the complicated large-amplitude motions exhibited in this system.

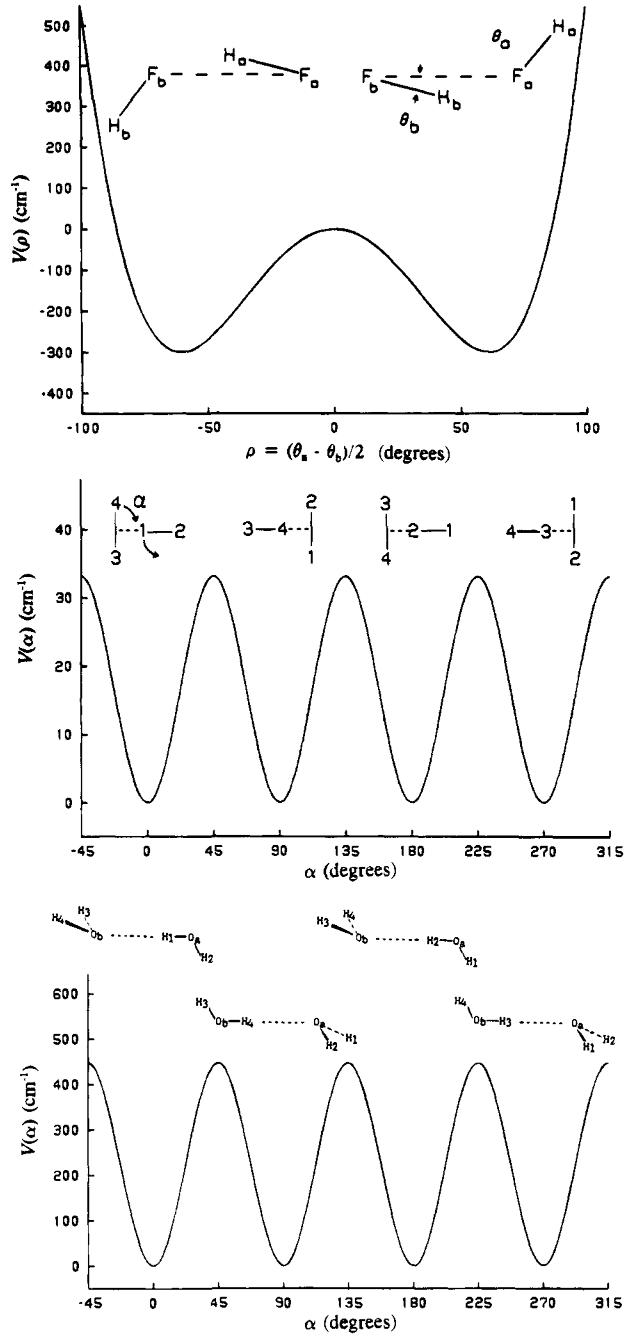


Figure 1. Tunneling motions in several weakly bound dimers.

Upon vibrational excitation of a monomer localized vibration in the dimers, these interchange tunneling splittings generally decrease significantly. For example, in $(HF)_2$ the tunneling splitting decreases from ~20 GHz to 6$-$7 GHz upon excitation of the proton donor and proton acceptor HF stretches.[58] This observation led Pine, Lafferty, and Howard[59] to suggest that the decrease in tunneling splitting arises because of the difficulty of exchanging the vibrational excitation between the monomer units, necessary in order that the tunneling leads to an isoenergetic configuration. Vibrational transition dipole$-$dipole coupling has been proposed as a mechanism for the vibrational energy interchange and a dynamical

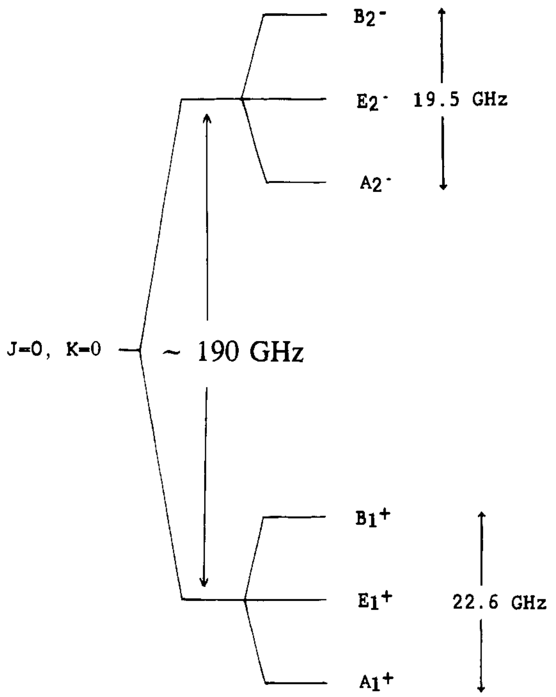


Figure 2. An energy level diagram of $(H_2O)_2$, illustrating the energy level splittings which arise from hydrogen interchange motions.

model on the basis of tunneling between degenerate local mode states has been developed to calculate the splittings.[77] The model has met with qualitative success in explaining the further drop in tunneling splittings for overtones of $(HF)_2$ and more recently with quantitative success in interpreting the splittings of the mixed overtone states. It also explains the tunneling–state selection rules for the C–H stretches of $(HCCH)_2$.[122] These selection rules, i.e. top–to–top and bottom–to–bottom or top–to–bottom and bottom–to–top in the tunneling splitting, cannot be derived group theoretically, but depend on the form of the model proposed for the vibrational exchange.

D. Tunneling Dynamics in Heterogenous Dimers

The intermolecular potentials of many weakly bound complexes are characterized by multiple minima separated by small potential barriers. When these minima are not isoenergetic and the potential barriers are sufficiently high compared with the zero point energy, isomers can result. Examples include N_2O–HF,[135–138] CO_2–HCN,[139–142] and HF-HCl.[143,144] When the minima are equivalent, tunneling between them can lead to significant complications in the rovibrational spectra. Nonetheless, with proper interpretation, valuable information about the barriers can be obtained. (See next section.) Among the types of motions which have been observed in heterogeneous dimers are hydrogen interchange tunneling in CO_2–H_2O,[145] nitrogen interchange tunneling in N_2–H_2O,[146] NH_3 internal rotation in NH_3–CO_2,[147] and CH_4 internal rotation in CH_4–HCl.[148] The motions are usually modeled as a hindered rotation of the monomer about one or more of its principal axes in a potential expanded in Wigner D functions or spherical harmonics, or represented as a Fourier series.

In stable molecules, the most well-studied motion is the internal rotation of a symmetric top, with methanol (for which the internal rotation barrier is ~375 cm^{-1}) being a classic example. In weakly bound dimers, the larger contact distances render the barriers significantly smaller, giving rise to values less than ~25 cm^{-1} in Ar–CH_3CN,[149] Ar–CH_3Cl,[150] Ar–NH_3,[151] Ar–$CH_3C{\equiv}CH$,[152] and HOH–NH_3.[153] Such facile internal rotation gives rise to strong Coriolis interactions which further complicate the spectra and lead to a large number of "forbidden" transitions.[150] Valuable information is contained in such spectra, however, as the Coriolis interactions are sensitive to the orientation of the top in the molecule, and thus provide information about the zero point direction cosines between the top axis and the inertial axes of the complex.[150]

In addition to internal rotation motions arising strictly from the van der Waals interactions, a number of complexes have also been studied in which one of the monomer units has its own internal rotation or inversion motion independent of complexation. Examples include the NH_3 umbrella inversion in ammonia complexes[91,98,154–156] and CH_3 internal rotation in methanol[157–159] and propene[160] complexes. The effects of complexation on these motions can be significant. For instance, in NH_3 complexes having a Lewis acid bonded to the NH_3 lone-pair orbital, the tunneling potential is asymmetric, and the inversion is effectively quenched. However, in the case of Ar–NH_3 states in which the Ar is localized perpendicular to the 3-fold axis, the tunneling splittings are within 5% of the free ammonia value.[154] This particularly unusual system is discussed further in the section on 3-fold internal rotation barriers.

E. Barriers to Internal Rotation

The existence of internal rotation in weakly bound complexes leads naturally to the question of measurement of barrier heights. It is interesting to note that an important reason to study internal rotation in valence bonded systems was to learn the nature of nonbonded interactions,[161] and this is, of course, at least as true for weakly bound systems. In the general binary complex, the six soft coordinates consist of one distance and five angles. Except for the simplest forms of atom–rod or rod–rod complexes, one coordinate at least will be regarded as an internal rotation coordinate. The treatment of internal rotation about a valence bond has a particular elegance, as the motion is one of large amplitude but the potential can be characterized by essentially only one parameter. In weakly bound complexes, however, there are a number of questions which arise before such a simple characterization is possible. For example, the axis about which internal rotation occurs is not generally obvious. Furthermore it is not clear that the assumption of rotation of tops at constant radial separation (as is the rule in valence bonded species) is valid. Nonetheless, with these qualifications in mind, the determination of barrier heights in weakly bound systems frequently follows the well-established methods of rotational spectroscopy, e.g., analyzing the differences of rotational constants of the different torsional species. In a few instances other properties such as dipole moments and differences in hyperfine structure may also be analyzed. Fortunately, for weakly bound complexes, the latter, to good measure, directly reflect the nuclear probability distribution and thus have simple and valuable interpretation.

1. Twofold Barriers

Twofold barriers pose distinct problems since the moments of inertia of the complex change as the internal rotation takes place. Yet, complexes with H_2O are frequently studied and the 2-fold barrier problem is therefore quite common. The two lowest energy rotational states of water, which are always present, are 0_{00} (with singlet proton spin function) and the 1_{01} (with a triplet proton spin function), and these lead to spatially symmetric and antisymmetric tunneling states, respectively, in the complexes they form. An important example of this type of system is the planar complex H_2O-CO_2,[145,162] point group C_{2v}, which is isoelectronic and isostructural to H_2CCF_2. The rotation is about the b inertial axis of the H_2O (i.e. the 2-fold axis), and the barrier is found to be 305(3) cm^{-1}. CO_2, a spinless molecule, follows Bose–Einstein statistics and thus, for the ground vibrational state, only even J rotational levels exist. The pure rotational spectrum[145] of the complex contains only even torsional levels for K even and only odd torsional levels for K odd. The A rotational constants are obtained for both series since the molecule is an asymmetric top, and their difference provides a measure of the barrier. Since the infrared allowed perpendicular vibrations produce an asymmetric H_2O molecule, the fine structure on the infrared[162] transition can directly provide the rotational level splittings and the internal rotation barrier, under the mild assumption that the latter is the same in both ground and excited vibrational state. It is impressive that the earlier, much more ambiguous barrier[145] is in perfect agreement with the much more reliable later determination.[162]

A closely related species is H_2O-N_2O. This is also a planar system, but it is bent 20° from a C_{2v} geometry,[163] thus giving the impression that the water has both oxygen interactions *and* a bent hydrogen bond with the oxygen of the N_2O. From such a structure one might expect the barrier to internal rotation to be appreciably higher than that in H_2O-CO_2, but the observed barrier of 235(10) cm^{-1} is, in fact, considerably less. The two systems are difficult to compare, however, as the internal motions must be somewhat different due to the C_{2v} and non-C_{2v} structures of the complexes. The complex $H_2O-NCCN$,[164] which *is* of C_{2v} symmetry, forms a better comparison with the CO_2 complex, but again, the measured barrier to internal rotation [285(6) cm^{-1}] is appreciably smaller. This is particularly interesting since the quadrupole moment of cyanogen is twice that of carbon dioxide, illustrating the subtleties which will arise in the interpretation of internal rotation barriers. It is interesting to note that the 2-fold internal rotation barriers in valence bonded species (e.g. ethylene) are generally quite high and that the 2-fold barriers discussed above, are also substantial fractions of the dissociation energy.

Complexes where water acts as a proton donor present a distinctly different type of double minimum problem. Here, the complexes have monodentate structures and undergo proton switching or hindered rotation about the c axis of water (i.e., the axis *perpendicular* to its plane).[146,165] The theory of the effect of internal rotation on the rotational constants for this type of system is likely to be extremely complex, depending upon intimate details of angular–radial potential. The complexes of water with CO and N_2 are examples. From the ^{14}N quadrupole hyperfine structure in N_2-H_2O, the average orientation of the N_2 molecule along the heavy atom axis is 23.2°.[166] (The corresponding angle is not well established for the CO, although in principle such a determination is possible with $C^{17}O$.) For the water subunit, however, the average orientation with respect to the heavy atom axis *can* be determined in *both* complexes from deuterium quadrupole coupling constants, and is found to be quite similar for the two species. The difference between the average rotational constants for the spatially symmetric and antisymmetric tunneling states of the two systems, however, differ by about a factor of 5. The two tunneling states in $CO-H_2O$ have been sufficiently studied that a barrier height of 210(20) cm^{-1} has been determinable. It appears that the available data for these systems are consistent with the reasonable expectation of a proton interconversion barrier in N_2-H_2O much lower than 210 cm^{-1}, but no precise determination has been made.

The motion of the N_2 moiety in the complexes N_2-H_2O and N_2-HF brings to light another interesting feature of 2-fold internal rotation and illustrates the subtlety which enters into determining even the most qualitative aspects of a system's internal dynamics. In N_2-H_2O, one sees unquenched internal rotation of the N_2,[146] while replacement of the H_2O by HF in the complex renders the two nitrogens completely noninterconverting[167] (as evidenced by their distinct values of eQq). Indeed, the effect is quite dramatic, as in N_2-HF the angular rigidity leads to a vibrationally averaged angle of only 16.8° for the bending of the N_2 away from colinearity with the HF. An appealing, but as yet untested explanation of the differing dynamics in the HF and H_2O complexes is that there is a geared motion in the latter in which internal rotation of the nitrogen is accompanied by a proton switching motion not possible in the HF complex. Perhaps even more dramatic than the effect of substituting H_2O by HF is the effect of isotopic substitution in $^{14}N^{15}N-H_2O$, in which the inequivalence of ^{14}N and ^{15}N is also enough to convert the system to a rigid noninterconverting structure.

2. Threefold Barriers

The 3-fold barrier to internal rotation is extremely well studied in valence bonded species. There are few examples of high 3-fold barriers in weakly bonded complexes, which is in accord with expectation from distance scaling. Comparison of NH_3-H_2O and NH_3-H_2S with CH_3OH and CH_3SH, where a hydrogen bond replaces the valence bond, is not quantitative since both the spectra of NH_3-H_2O and NH_3-H_2S and their fully deuterated isotopomers are fit by free internal rotation with unfortunately very large upper limits for the barriers.[168] Splittings due to proton switching in H_2O and H_2S are also observed, however, giving tunneling splittings of 56.5(15)[153] and 864.4(2) MHz[169] for the H_2O and H_2S systems, respectively.

An interesting internal rotation problem virtually unique to van der Waals molecules is found in the complexes Ar–CH_3Cl,[150] Ar–CH_3CN,[149] and Ar–NH_3,[170] alluded to earlier. In Ar–CH_3Cl the heavy atoms form a T-shaped structure[150] with the Ar located about 3.750(1) Å from the carbon atom. Since CH_3Cl is relatively heavy, "in-plane" zero point oscillations are not large. Although the T-shaped heavy atom structure remains intact throughout the zero point motions, the CH_3Cl internally rotates about its C_3 axis, and the upper limit for the barrier to this motion has been placed at about 20 cm^{-1}.

A more extreme case is the highly nonrigid species Ar–NH_3, where rotation about all *three* axes of the NH_3 is nearly unhindered. The nonrigidity is clearly seen in the hyperfine structure for the lowest state of the complex, which correlates with $J = 0$ of free NH_3, and is born out by a host of other spectroscopically measured quantities. The average internuclear separation in all of the above states appears quite constant at approximately 3.8 Å, and the intermolecular stretching states for both $K = 0$ and $K = \pm 1$ type states have been observed. The polar angle dependence of the 3-fold internal rotation barrier has been determined,[151] varying (obviously) from zero, in either of the symmetric top configurations, to approximately 25.6(2) cm^{-1} in the vicinity of the equilibrium, near perpendicular geometry. A very complete data set now exists for this system,[91,151,154,155,170–174] and recent multidimensional dynamical analysis has been used to fit a potential surface to the spectroscopic data, thus providing the most detailed knowledge of the intermolecular potential currently available.[175]

Studies on methanol complexes[157–159,176] have led to some interesting discussion regarding the effect of weak bond formation on the internal rotation barrier within a subunit of the complex. For instance, in the methanol complex with formamide, which has a planar heavy atom structure with NH––O- and OH––O=C< hydrogen bonds, the internal rotation split A and E symmetry rotational transitions imply a 3-fold barrier decrease of approximately 140 cm^{-1} from that of the monomer.[158] A pleasing physical picture has been developed to rationalize this reduction in terms of a gradual change of the 3-fold potential to a 6-fold potential as the local symmetry around the CH_3OH oxygen atom increases.[158] Casting doubt on this picture, however, are recent results on CO–methanol,[176] which show an even more dramatic barrier lowering of nearly 200 cm^{-1} even though the interaction is presumably weaker than in methanol–formamide, and does not show the analogous symmetry increase. It has been recently suggested[177] that these apparent decreases in internal rotation barriers are artifacts of the analysis which neglects the large zero point oscillation of the OH group in the complex. Instead of invoking such dramatic barrier decreases to interpret the A/E torsional splittings in the microwave spectrum, they are attributed to a zero point reduction in the reduced mass for tunneling. The propene–SO_2 complex[178] which does not have a light rotor, such as the OH group in CH_3OH, does not exhibit any appreciable change in the 3-fold barrier upon complexation when the spectra are analyzed in a manner similar to that initially applied to formamide–methanol and CO–methanol.

F. Determination of Globally Reliable Potentials

The promise of the spectroscopy of weakly bound complexes has been to provide reliable intermolecular potentials. From the early pure rotational spectroscopy, a picture of likely equilibrium configuration plus zero point oscillation amplitudes was obtained. Considerable progress through measurements of the soft mode vibrations has greatly enlarged the portion of configuration space that the molecules sees.[21,22] This, together with soft mode combination bands seen in valence bond excitations, has given as large a data set with respect to configuration space as exists for any polyatomic system. A rotational Rydberg–Klein–Rees (RKR) analysis has been applied to determine radial potentials in a few cases,[167b,179] but a fully dimensional RKR method for direct inversion of spectral data has not been demonstrated. Thus, the generation of the intermolecular potential requires a flexibly parameterized potential whose coefficients are in general adjusted to the experimental data set by nonlinear least squares. Indeed, a considerable effort has been expended toward achieving a stable representation for such multicoordinate potentials. Global potentials for Ar–HF[180a] and Ar–HCl[180b] have been developed; the H–X coordinate is, however, the vibrational average interaction energy rather than the explicit distance. Similar but clearly more complex potentials have been developed for Ar–H_2O[181] and Ar–NH_3.[175] For the latter, only the ground valence vibrational state of the hydrides are considered. Several excellent reviews describing the methodology and successes in determining globally reliable potentials are available elsewhere.[18,19,22]

G. Vibrational Dependence of the Interactions

The large experimental effort in the near-infrared to study the monomer-localized fundamental vibrations[15] in weakly bound complexes has recently been extended to overtone vibrations to allow a more complete understanding of the vibrational dependence of the interactions. High-resolution overtone studies have been reported on the HF stretches of $(HF)_2$[75,78,80] and Ar–HF,[182–184] the C–H stretches of HCN–HF,[185] $(HCN)_2$,[186] and BF_3–NCH,[187] and the NO stretches of $(NO)_2$.[188] In some cases, such as Ar–HF, combination vibrations have been observed, giving detailed information about the coupling of the monomer coordinate to the dimer coordinates. The most extensive experimental data is available for Ar–HF and $(HF)_2$ for which the $v = 0$, 1, 2, and 3 HF stretches have been characterized.

In Ar–HF,[182–184] it is found that the frequency shift of the HF stretch increases slightly faster than linearly with increasing number of HF quanta. By $v = 3$ the zero point binding energy of Ar–HF has increased by ~33% over the ground state value. Concomitant with this increased binding energy is a decrease in both the interaction distance and the HF bending amplitude, as seen by examination of the rotational constants, electric dipole moments, and van der Waals frequencies of the excited vibrational states. Despite the fact the coupling strength of the monomer mode to the van der Waals interaction is a significant fraction of the van der Waals binding energy, the vibrational predissociation rates for Ar−HF are significantly smaller than those typically observed for weakly bound complexes. The $v = 1$ excited complex is found to live longer than 0.3 ms[189] and the $v = 3$ excited complex has a lifetime of greater than 80 ns.[184a] Precise measurements of vibrational predissociation widths for the Ar−HF vibrational states would be valuable to assess the utility of this information in improving on the repulsive part of Ar−HF pair potential. Also, the effects of the increased number of open channels and the better coupling of the HF stretch to the van der Waals coordinate due to the reduced zero point bending amplitude can be explored.

An even richer vibrational dynamics is observed in the overtone spectra of $(HF)_2$.[75,78,80] The vibrational predissociation rate is found to be mode K and tunneling state dependent. The faster predissociation rate for the proton donor HF unit has been rationalized[67a] in terms of better kinetic coupling of the HF stretch to the dissociation coordinate. Photofragment studies on the fundamental bands[190,191] verify this picture and show the importance of near resonances in the dissociation process. Also, as with the Ar−HF studies, we see a significant increase in the van der Waals binding strength with vibrational excitation.[75,78,80] Experimentally, the dynamics of $(HF)_2$ are well characterized, but the system is sufficiently complicated to have eluded any accurate theoretical description. It is expected that $(HF)_2$, as a prototype interaction between two linear molecules, will generate much theoretical interest in the years to come.

H. Realistic Measurements of Dissociation Energies

High-resolution microwave studies of weakly bound complexes give detailed structural and dynamical information about the region near the bottom of the ground state potential well. The most important information about the *top* of the well, however, (i.e., its location) is not determined from such experiments. Fortunately, a number of methods have been successfully used to measure van der Waals dissociation energies, and some examples are presented in this section.

One of the earliest spectroscopically based measurements of a van der Waals dissociation energy was that of HCN−HF [1542(92) cm^{-1}], done by Legon and co-workers in 1978.[192] Absolute transition intensities in a Stark modulated microwave cell spectrometer were made under thermal equilibrium conditions, and knowledge of the absolute rotational line strengths and number densities of the monomers allowed calculation of a "vibronic ground state equilibrium constant", $K_{00} = n_{v=0,J=0}(\mathrm{HCN{-}HF})/n_{00}(\mathrm{HCN})n_{00}(\mathrm{HF})$. Since the measured "equilibrium constant" in this case applied specifically to the vibronic ground state, it could be readily related to the dissociation energy, D_0, according to $K_{00} = Q_{AB}/Q_AQ_B \exp(D_0/kT)$, using only translational partition functions, Q_i. Thus, the analysis did not depend on the internal structure of the three species and was particularly simple. Analogous methods have been used in the infrared, and high-resolution measurements of integrated absolute infrared line strengths have yielded D_0 for the complexes $(HF)_2$ [1038(+43/−34) cm^{-1}],[193] $(HCl)_2$ [431(22) cm^{-1}],[193] and $(NO)_2$ [639(35) cm^{-1}].[194,195] Here, the analysis is quite detailed and requires careful attention to line profiles and the complete partition functions of the monomers.

The observation of rotational predissociation has also successfully yielded weak bond dissociation energies. Howard and Pine, for example, have determined the binding energy, D_0, of Ar−HCl to be 114.7(10) cm^{-1},[196] and Fraser and Pine, using the same technique, have obtained binding energies of 101.7(12), 133.0(12), and 180.9(22) cm^{-1}, for Ar−HF, Kr−KF, and Xe−HF, respectively.[197] Infrared absorption spectra were recorded in a cooled White cell containing a 10% mixture of HF in 2000 Pa (15 Torr) of the rare gas. Higher J rotational levels of the complexes were missing due to rotational predissociation, which occurs when the rotational energy exceeds the binding energy and when tunneling through the centrifugal barrier is fast enough to produce noticeable spectral broadening. The authors argued that the use of pseudodiatomic radial ptoentials to model the potential surface is equivalent to averaging the complete anisotropic potential over the librational motion of the HX subunit. A one-dimensional, four-parameter, Maitland−Smith potential (a generalization of the Lennard-Jones form) was assumed, and the ground and excited state potential parameters adjusted to reproduce the spectra, the red shift (from monomer HX), and the line widths (calculated from tunneling).

Similarly, Lovejoy and Nesbitt have determined the binding energy, D_0, of Ne−DF to be 34.7(8) cm^{-1},[198] of He−HF to be 7.1(1) cm^{-1}, and of He−HCl to be 10.1(12) cm^{-1}.[199] Here, a slit nozzle, with its gentle density decrease, going as (distance from slit)$^{-1}$ is used to produce these extremely weakly bound species. Presumably, the slit nozzle is efficacious in the production of these complexes because all the molecules spend more time in regions of densities high enough for the cooling three-body collisions to occur. Direct absorption of near infrared radiation was monitored to produce vibrational−rotational spectra in which the HX moiety is vibrationally (and internal rotationally) excited within the complex. For the helium-containing systems, a cutoff was observed in the end-over-end rotational progression of the complex due to rotational predissociation in the vibrationally excited state (as opposed to the vibrational ground state, as was the case in the Fraser and Pine studies). Here, a Lennard-Jones-like $(m,6)$ potential form was assumed. The line widths are extremely sensitive to the energy level position within the centrifugal barrier and thus precisely define the excess energy above dissociaiton. The fitting procedure of Fraser and Pine was used and simple changes in the assumed form of the potential produced negligible differences in the dissociation energy.

Vibrational predissociation in optical spectra has also been used by Janda and co-workers to measure the ground state dissociation energies of a number of rare gas–halogen complexes.[200–202] The measurements are made by a pump–probe technique in which the complex dissociates following initial electronic excitation into the B state of the halogen moiety. A second laser further excites the electronically excited free halogen resulting from the dissociation, and total fluorescence is monitored. Thus, the nascent distribution of rotational and vibrational levels of the halogen molecule produced by the dissociation process is interrogated. The van der Waals dissociation energy of the electronically excited $Ar-X_2$ complex is bracketed by noting the largest value of j, the rotational quantum number of B state of the halogen, for which the dissociation terminates, and by then applying energy conservation, with the centrifugal barriers and conservation of angular momentum also taken into account.[201] By correcting for the blue shift of the X → B transition for $Ar-X_2$ compared to X_2 itself, the dissociation energy of the ground electronic state of the complex is determined. Since j_{max} is typically around 25, the accuracy with which the dissociation energy can be bracketed is characteristically 8 $cm^{-1} \approx 2j_{max}B(Cl_2)$ [where $B(Cl_2)$ is the rotational constant of the B state of Cl_2]. Some values determined in this way are[200–202] $He-Cl_2$ [10(3) cm^{-1}], $Ne-Cl_2$ [30(3) cm^{-1}], $Ar-Cl_2$ [185(1) cm^{-1}], $Ne-Br_2$ [70(2) cm^{-1}], $He-I_2$ [18(5) cm^{-1}], $Ne-I_2$ [75(5) cm^{-1}], $Ar-I_2$ [235(5) cm^{-1}], Ne–ICl [70(5) cm^{-1}], Ar_2Cl_2 [447.5(35) cm^{-1}], Ar_3-Cl_2 [776(3) cm^{-1}], $Kr-Cl_2$ [236.6(20) cm^{-1}], and $Xe-Cl_2$ [286.3(11) cm^{-1}].

Perhaps the most accurate dissociation energy determinations come from recent state-to-state photofragmentation experiments. Dayton, Jucks, and Miller have measured the dissociation energy of $(HF)_2$ to be 1062(1) cm^{-1},[190,191] an increase in accuracy of a factor of 40 over the integrated infrared intensity measurements. An F-center laser vibrationally excites $(HF)_2$ in a beam which is monitored with a bolometer detector. Upon resonance, the dimer predissociates causing the HF fragments to recoil out of the beam, and the event is recorded as a change in translational energy transferred to the detector. By rotation of the bolometer about the laser/beam interaction region, the HF photofragment angular distribution can be measured. The rotational states of the recoiling HF monomers are well separated in energy and both fragments are in their ground vibrational levels. The possible relative translational energy of the fragments are quantized by conservation of energy, which results in a Newton sphere with a well-defined radius for each rotational channel for predissociation. Thus, in the laboratory frame there is a maximum scattering angle (for each rotational channel) which is dependent upon D_0, and which can then be determined by adjusting it to fit the observed angular scattering pattern. $Ar-CO_2$, with a dissociation energy of 166(1) cm^{-1}, has also been studied by this photofragmentation technique.[203]

I. A New Look at the Simplest Systems: Rare Gas Dimers and Related Species

As the complexity of accessible systems has increased, a recent set of experiments has returned to examining the very simplest of prototypes for weak intermolecular interactions, the rare gas dimers. By incorporating sizable microwave amplification into a pulsed nozzle Fourier-transform microwave spectrometer, Gerry and co-workers have been able to study such small dipole moment systems as Ne–Kr,[204] Ne–Xe,[205] Ar–Kr,[204] Ar–Xe,[205] Kr–Xe,[205] Ne_2-Kr,[206] and Ne_2-Xe.[206] A number of rare gas complexes with nonpolar diatomics, viz. $Ar-N_2$,[166] $Ar-Cl_2$,[54] Ar–CO,[207] $Kr-N_2$,[208] and $CO-Cl_2$[209] have been studied by this group as well, and all except the linear $CO-Cl_2$ have T-shaped geometries. Hg–Ar has also been studied by Oshima et al.[210]

For the rare gas dimer systems, only the ground vibrational states were measured, but the equilibrium bond lengths, r_e's, were estimated using the abundance of available isotopic data. This provides a particularly clean comparison with the best available potentials for these systems and gives results which are in reasonable agreement with the literature values (although systematically larger by about 0.02–0.03 Å). Harmonic vibrational frequencies and force constants were also estimated from centrifugal distortion data. The force constants were found to roughly parallel the dissociation energies, with that of Ne–Xe < Ar_2 < Kr_2 < Ar–Xe < Kr–Xe, although interestingly, the ordering is switched relative to the dissociation energies for Kr_2 and Ar–Xe.

Some particularly interesting information about electronic rearrangement was also obtained for these systems. By measuring the microwave pulse length required for spectral optimization, (i.e., that needed to create an exact $\pi/2$ pulse), Jäger et al. have been able to give preliminary estimates of the dipole moments of Ne–Kr (0.010 D),[204] Ar–Kr (0.004 D),[204] Ne–Xe (0.012 D),[204,205] Ar–Xe (0.014 D),[204,205] and Kr–Xe (0.007 D).[204,205] Nuclear quadrupole coupling constants for ^{131}Xe in Ne–Xe, Ar–Xe, and Kr–Xe were also measured[205] (directly from spectral frequencies). Since the free ^{131}Xe atom is in the ^1S state (with no electric field gradient at the nucleus), the nonzero quadrupole coupling constant is a clean measure of the electronic distortion associated with van der Waals bonding in these (almost) nonpolar dimers. The quadrupole coupling constant of atomic ^{131}Xe in the $5p^56s$ $(^3P_2)$ state is −883.8 MHz[211] and corresponds to the electric field gradient at the nucleus when one full p electron is missing from the xenon atom. Even if interpreted strictly as charge transfer, the $eqQ(^{131}Xe)$ in $^{20}Ne-^{131}Xe$ (+0.3878(9) MHz) would represent only 4×10^{-4} of a p electron transferred *into* the Xe atom from the Ne atom. The measured ^{131}Xe quadrupole coupling constants are remarkably large, in a sense, as their magnitude is about 10% of that in Xe–HX complexes. (The sign, however, is opposite.) It is clear that even nonmultipolar interactions can produce substantial electronic rearrangement in these systems.

A particularly significant (albeit nonspectroscopic) experiment pertaining to the simplest of rare gas dimers is also worthy of note. Luo et al.[212] have recently observed $^4He_2$ by electron impact ionization of a 1 mK supersonic expansion of helium. This brings to rest a long standing controversy over the existence of this species, whose zero point energy is so close to the dissociation limit that only the $v = 0$ $J = 0$ level exists, and that even the isotopomer $^3He-^4He$ is not bound. The vibrational wavefunction is astonishingly delocalized with $\langle R \rangle > 50$ Å and a significant amplitude at internuclear separations as large as 200 Å! At such large distances, relativistic contributions to the dispersion energy become significant due to the finite time needed to propagate the electric field arising from instantaneous fluctuating dipoles. The influence of this "retardation" effect on the nature of He_2 has been examined.[213]

III. Larger Clusters

A. Overview

It has always been an explicitly stated goal of work on weakly bound complexes to "bridge the gap" between a detailed understanding of isolated dimeric interactions and our less complete knowledge of bulk phase structures and properties. Significant progress has been made in recent years via the enunciation of the structures of trimeric, tetrameric, and even pentameric weakly bound complexes. By and large, this has been accomplished by exploiting the extreme sensitivity of the time-domain technique of pulsed-jet Fourier-transform microwave spectroscopy, though infrared and far-infrared techniques, as well as fluorescence spectroscopy has also made important contributions. An impressive variety of complexes has now been examined. Systems with several rare gas atoms bound to another entity are the simplest and include Ar_nHX ($X = F$, $n = 2-4$;[214–217] $X = Cl$, $n = 2,3$[214c,218–220]), Ar_2CO_2,[221] Ar_2OCS,[222] and Ar_2-HCN.[223] Electronic spectroscopy, although outside the scope of this review, has made numerous contributions here as well, with Rg_2Cl_2 (Rg = He,[224] Ne[225]), $He_2R-C_5H_4$ (R = H, CH_3[226]), and $Ar_2C_6H_6$[227] being but a few representative examples. In addition, a wide variety of "polymolecular" trimers and tetramers containing HCN[228–231] or the $(HCN)_2$ unit[232–234] have been studied, as have mixed clusters of H_2O with CO_2.[235,236] Several homogeneous trimers such as $(HF)_3$,[237] $(DF)_3$,[238] $(D_2O)_3$,[239] $(H_2O)_3$,[240] $(CO_2)_3$,[241] and $(HCCH)_n$ ($n = 3-5$)[242–245] have also been examined at high resolution. A more complete listing of systems investigated is available elsewhere,[26] and some representative structures are shown in Figure 3. With the study of these species, a level of complexity unthinkable just a few years ago has been attained, as is illustrated by systems such as $H_3N-HCN-HF$[231] and $(CO_2)_3-HCN$[230] whose structures have been successfully elucidated by microwave spectroscopy. Clearly, a comprehensive discussion of these species, even at the most cursory level, is beyond the scope of this review, but several systems serve to highlight the types of issues that arise.

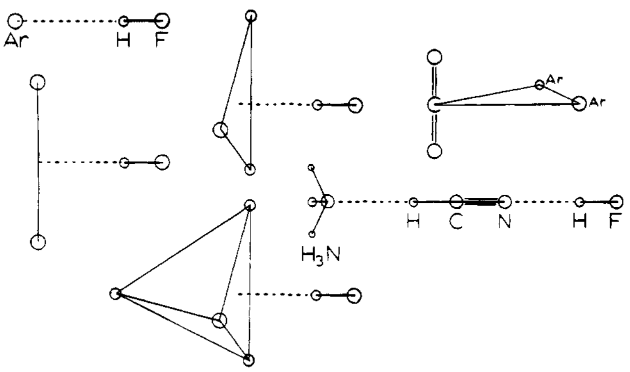


Figure 3. Several representative structures of weakly bound trimers studied by microwave spectroscopy. The atoms in the Ar_n-HF complexes are left unlabeled for $n > 1$ for the purpose of clarity. References to the original works are given in the text.

The first microwave studies involved the sequential complexation of additional rare gas atoms to the prototypical van der Waals complexes of Ar–HF and Ar–HCl to produce Ar_2HF,[214] Ar_3HF,[216] Ar_4HF,[217] Ar_2HCl,[218] and Ar_3HCl.[220] The Ar_2HX complexes are planar, C_{2v} systems with the hydrogen directed along the bisector of the Ar–Ar bond. Not too surprisingly, in Ar_3HX, the argons form an equilateral triangle, and the HX hydrogen bonds perpendicularly to its face. A fourth argon atom bonds to Ar_3HF on the face of the Ar_3 opposite the HF. A central question in the study of larger clusters is the validity of the additivity approximation for intermolecular potentials. The simplest (and most simplistic) picture of the structures of large clusters is that of "dimers within trimers", and it is of interest to compare, for example, the Ar–Ar distances in the Ar_n-HX complexes with that found in Ar_2, or the Ar–X distance with those of Ar–HF or Ar–HCl. To the extent that intermolecular potentials are additive and that geometry allows, one expects approximately equal atom–atom distances, independent of the degree of complexation with other species. This is found to be approximately the case for the Ar_nHX systems, with only a slight (a few hundreths of an angstrom) lengthening of the Ar–Ar bond over that of Ar_2. It is interesting to note that an harmonic force field analysis of centrifugal distortion data for both Ar_2–HF and Ar_2HCl indicates an Ar–Ar stretching frequency which is about 10% lower than that in free Ar_2.[214b,218] A somewhat more surprising result is the virtual constancy of the average HF angular excursion in the series Ar_nHF ($n = 1-4$) despite the varying number and location of argon atoms. (This constancy, however, does not carry through to the DF species.) The Ar_nHF systems have also been investigated in the infrared, but discussion of those results is deferred to a later section.

In a similar spirit, the systems Ar_2-CO_2[221] and Ar–OCS[222] have been examined by microwave spectroscopy. Both $Ar-CO_2$ and Ar–OCS are T-shaped species and thus are able to accept a second argon without imposing additional geometrical constraints on the Ar–C or Ar–Ar distances. To a good approximation, the structure of Ar_2-CO_2 is that of an Ar_2 bound to CO_2, with each $Ar-CO_2$ structure[246] fully respected. The complex has C_{2v} symmetry, with the $D_{\infty h}$ axis of the CO_2 perpendicular to the plane of the isosceles triangle formed by carbon and the two argons. The Ar–C–Ar angle is 66°, with an Ar–Ar distance of 3.8431 Å (compared to 3.822(22) Å in Ar_2[247]). Moreover, the two Ar–C distances are 3.508

Å, which is quite close to the 3.5048(1) Å weak bond length in Ar–CO_2.[246] Interestingly the Ar–Ar stretching frequency in the trimer, 23.5 cm^{-1}, also compares very favorably with the 25.69(1) cm^{-1} value in Ar_2. Qualitatively similar results are found for Ar_2OCS.[222]

Somewhat larger structural differences have also been observed. $(HCN)_3$, for example, has been studied in the microwave[232b] and in the infrared.[232a] Two isomers have been observed, a linear HCN–HCN–HCN (seen in both the infrared and the microwave) and a nonpolar cyclic form (seen only in the infrared). In the linear species, the weak bonds are contracted by 0.06 Å and 0.05 Å relative to $(HCN)_2$ for the "left" and "right" weak bonds as written above. The dipole moment of $3.54(3) \times 10^{-29}$ Cm [10.6(1) D] is enhanced 6.0×10^{-30} Cm (1.8 D) over the vector sum of the three vibrating monomers (2.95×10^{-29} Cm = 8.83 D), but the enhancement is entirely consistent with that predicted from electrostatic moments and polarizabilities. It is interesting to note that CO_2, HCN, HCCH, and H_2O all form cyclic trimers, even though the dipole moments of these species vary from 0 to 1×10^{-29} Cm (3 D).

B. Quantitative Probes of Nonadditive Interactions

The structures of higher clusters clearly provide new insights into many body interactions. Structures alone, however, only hint at *energetics* which where the essence of the additivity approximation lies. Moreover, it has been aptly noted[235a] that even in the hypothetical case of only pairwise interactions, it may be geometrically impossible for trimers to faithfully adhere to dimeric structures, so that differences in bond distances and angles between dimers and trimers may not, of themselves, signal cooperativity. This situation has the advantage, though, of allowing the exploration of regions of the potential not easily accessed by vibrational excitation.

Historically, the investigation of nonadditive interactions has focused on bulk measurements from which the extraction of microscopic information is indeed a difficult problem. Consequently, many workers have turned to *ab initio* quantum chemistry to fill the need for quantitative information about deviations from pairwise additivity. The rare gas trimers, e.g. He_3,[248] Ne_3,[249] and Ar_3,[250] as well as other simple "closed shell" atomic systems such as Be_3[251] have been investigated. Molecular systems, though more difficult, have also been studied by *ab initio* techniques. Examples include $(HF)_3$ and $(HCl)_3$,[252] $(H_2O)_3$,[253] $(NH_3)_3$,[254] and $(CH_4)_3$.[255] Several reviews on nonadditivity are available.[256]

What are probably the most quantitative experimental studies to date, however, have only recently appeared. In a particularly definitive series of papers by Saykally and co-workers,[219] paralleled by state-of-the-art theoretical work of Hutson et al.,[257] the accurately known Ar–Ar[258] and Ar–HCl pair potentials[259] were exploited to explicitly and quantitatively test the additivity approximation in the complex Ar_2-HCl. After the original microwave work by Gutowsky and co-workers,[214c,218] Hutson et al. showed that, although the microwave spectrum of the ground state indeed contained information about three-body terms, observation of the intermolecular vibrations were necessary before their effects could be reliably assessed.[257b] Three intermolecular bending states were subsequently measured by far-infrared spectroscopy[219] and the results thus compared with predictions generated from a purely pairwise additive potential.[257a] The calcultions indeed showed measurable deviations from experiment which could not be ascribed to computational inaccuracy or deficiencies in the Ar–HCl pair potential. The effects of nonadditive interactions, however, could account for a substantial part of the discrepancies. The interaction between the exchange quadrupole moment of the Ar_2 moiety and multipole moments of the HCl was found to be the most significant three-body term, and its inclusion gave substantially improved (although still not perfect) agreement with the spectroscopic data. In contrast, while the triple dipole interaction, the induced dipole–induced dipole interaction, and the exchange overlap contributions were significant, none was sufficient to account for experimental observations. It is interesting to note, too, that the far infrared data reveal a significant coupling between the motions of the Ar_2 moiety and those of the HCl.[219b] This directly indicated the need to treat all of the soft degrees of freedom in calculating the spectrum, thus forcing the abandonment of the "reverse adiabatic" approximation employed in earlier theoretical work. The need to explicitly treat all five low-frequency motions certainly demonstrates the dynamical complexity possible in even the simplest of higher clusters!

Along parallel lines, an elegant series of experiments by Nesbitt and co-workers[215] have examined the HF stretching vibration in the complexes Ar_nHF (n = 1–4). The incremental red shift in the HF stretching frequency for each member of the series depended primarily on its position with respect to the average direction of the HF dipole moment in the complex and could be reasonably accounted for by simple models based on two body effects. A significant radial dependence is also indicated by a negligible (<2%) shift resulting from the addition of the fourth argon atom, which situates on the face of the Ar_3 triangle, opposite the HF. By $n = 3$, nearly half the shift observed in matrix isolated HF was obtained.

In a subsequent paper, the same group performed classical and quantum mechanical calculations on these systems in using a strictly pairwise additive potential.[260] The lowest energy structures correctly corresponded to those experimentally determined and a number of isomeric forms not yet observed were also predicted. Although the correct experimental structures were obtained, however, the use of the additivity approximation was found to predict an angular anisotropy for the HF in these systems which steadily increased with cluster size. This latter feature is in direct contradiction to spectroscopic results, indicating that three-body terms may account for the surprising constancy in the angular anisotropy of the HF noted above. As in the case of Ar_2-HCl, significant coupling of the Ar–Ar stretch, the Ar_n–HF stretch, and the bending of the Ar–Ar subunit was indicated, again underscoring need to explicitly treat all intermolecular coordinates for these types of systems before quantitative comparisons with spectral data can be made.

It seems clear that the nature of the nonadditive terms will be system dependent and that a substantial cross section of the diverse set of possible interacting systems will need to be examined before a full understanding of three- and higher-body interactions is achieved. Nonetheless, the above infrared and far-infrared studies represent the first truly precise, quantitative, experimental interrogation of nonadditive effects. Indeed it is encouraging that the experimental and theoretical tools developed for dimeric systems have matured to the point that progress toward the detailed understanding of condensed systems is truly in sight.

C. Tunneling Dynamics in Larger Clusters

Studies of larger clusters present the opportunity for even richer tunneling dynamics due to the greater number of equivalent or nearly equivalent minima which are possible. In addition, the apparent propensity of larger clusters to form cyclic geometries offers the chance to study new types of large amplitude motions such as ring puckering and pseudorotation. In $(D_2O)_3$, for example, 96 tunneling pathways are possible, including motions which interconvert right- and left-handed enantiomers of this chiral complex.[239] The potential for many of the homogenous trimers and larger polymers to be nonpolar complicates these studies by preventing higher resolution microwave studies necessary to resolve very small tunneling splittings. In some cases, such as in $(HF)_3$, small centrifugally induced dipole moments give rise to a pure rotational spectrum, but such transitions have not been observed for any of the cyclic trimers or tetramers. The recent successes in observing pure rotational transitions for the extremely weakly polar Ne–Xe, Ar–Xe, and Kr–Xe[205] suggest the possibility of future measurement of rotational transitions for the cyclic $(HF)_3$ and $(HF)_4$.

Perhaps the most characterized of the large cluster systems are those involving HCCH where high-resolution spectra have been reported for the dimer through the pentamer.[120–122,124,125,242–245] The dimer structure is found to be T-shaped[120–122] and the trimer through pentamer[242,245] are cyclic. For the larger HCCH clusters, the possibility of isomers has not been well addressed experimentally due to limited signal-to-noise ratio. In these systems as well as in other larger cluster systems, there is an inherent experimental bias toward isomers which have high symmetry since the spectra for symmetrical complexes have many overlapping transitions which effectively increase the signal-to-noise ratio. This might explain why the experimental molecular-beam infrared spectrum of the pentamer gives a cyclic geometry,[242b] while *ab initio* calculations suggest a noncyclic C_{2h} minimum resembling the structure of two cyclic C_{3h} acetylene trimer sharing a common acetylene unit.[261]

The infrared spectra of the acetylenic-like asymmetric C–H stretch of the tetramer suggests a rigid cyclic complex.[242b] The spectroscopic constants have been interpreted in terms of a nonplaner puckered-ring geometry with S_4 symmetry. However, *ab initio* calculations by Bone et al.[261] lead to an alternative interpretation of the infrared spectrum. Their calculations suggest that the minimum energy configuration is C_{4h} instead of S_4, with an extremely low frequency out-of-plane ring puckering vibration. This low-frequency mode may be complicating the structural interpretation of the tetramer spectrum. It is interesting to speculate that the apparent S_4 structure found experimentally may be the result of a slight dynamical stabilization of the S_4 configuration over the C_{4h} configuration upon excitation of the C–H stretch. Similar dynamic effects have been proposed to explain the observed dipole moment for the "C_{2h}" $(NH_3)_2$.[262]

IV. Modeling the Interactions

From a practical standpoint, an important goal of the study of intermolecular forces is the development of accessible means of predicting the nature of intermolecular interactions in systems which have not been previously studied, or which are intrinsically too complicated to calculate from first principles. *Ab initio* theory has made significant progress in small to moderate sized complexes, but noteworthy problems still exist. Electrostatic modeling is inherently less correct, but offers a real alternative, with relatively little restriction imposed by the size of the system.

A. Electrostatic Models

The crudest chemical approach to potential modeling the attractive part of an intermolecular would be the assignment of partial charges to the constituent atomic centers. The crudest physical approach would be the use of the first few terms in a multipole expansion to describe each molecular charge distribution. In 1981, Stone advanced a combination of these approaches,[263] in which a multipole expansion centered at *each* atomic site is used. Additional multipoles may also be placed at bond centers as needed. Such a distributed multipole analysis (DMA) enjoys the advantage of more rapidly converging to an approximation of the electric field about a molecule. The multipoles are calculated so as to reproduce the *ab initio* charge distribution and thus, in a sense, the method amounts to an efficient encoding of the true charge density, which need only by calculated once for each monomer.

The surface of convergence for the electric field resulting from the distributed multipoles is tight enough to be useful for pairs of molecules involved in weak complexation. The method can certainly be criticized on fundamental grounds,[264] as it is clear that any partitioning of the exact Hamiltonian for a van der Waals complex will involve some terms other than purely electrostatic ones (see for example ref 265). Nonetheless, the DMA charge distribution, coupled with an arbitrary repulsive surface does surprisingly well at reproducing geometries and induced electrostatic moments of many weakly bound complexes. Indeed the electrostatic description of weak interactions has become something of the language of choice, at least for the more strongly bound systems, and appears to have largely replaced the older HOMO/LUMO picture (see, for example, refs 48 and 266). The latter, of course, in its usual application, does not involve computation of optimum structures, although it is worth noting that it still provides qualitative insights useful to some. Quantitative aspects of this more chemical viewpoint have also been developed.[11]

Many of the first successes of the DMA electrostatic models were presented by Buckingham and Fowler in 1985.[267] In that work, a short–range repulsion, represented as hard spheres, was added to the potential. Equilibrium structures were calculated by a minimization of the electrostatic interaction energy subject to the constraint of the hard spheres; no polarizabilities were included. Structures were deduced for 29 complexes and found to be in essential agreement with experiment. For example, the complex between HF and formaldehyde is experimentally determined to have the HF hydrogen bonded to oxygen with a C—O—F angle of 109.5° and an O—F distance of 2.66 Å.[268,269] Buckingham and Fowler find this qualitative structure with an angle of 110° and an O—F distance of 2.75 Å, set by their rather unforgiving hard spheres. One might expect a hydrogen bonded complex to be well modeled by this method, but even a non-hydrogen bonded example, the skewed parallel structure of the $(CO_2)_2$ is qualitatively predicted with a C—C—O angle of about 70°. The experimental value (determined some time after the prediction) was found to be 58.2(8)°.[270–272]

Missing from this model is the inclusion of polarizability, and there is also the troubling problem of the arbitrary short-range repulsive addition to the potential. Distributed polarizabilities were introduced by Stone in 1985.[273] Spackman has introduced a rational method of modeling the shorter range terms in the potential in terms of atom–atom potentials,[274] and has successfully applied his method to hydrogen bonded complexes.[275] Dykstra has similarly modeled the short range terms with an "augmenting potential" which is Lennard-Jones-like and is based on combining rules over individual atom-associated constants.[276,277] Rather than using the distributed multipole approach, however, Dykstra includes in the electrical part of the potential properties like the single center multipoles, the dipole polarizability (energy response to the square of the electric field, **E**), the dipole–quadrupole polarizability (energy response to the product $\mathbf{E}\nabla\mathbf{E}$), the quadrupole polarizability (energy response to the square of $\nabla\mathbf{E}$), and the dipole hyperpolarizability (energy response to the cube of **E**). This model reproduces, for example, the correct structures for Ar_3–HF and Ar_4–HF with the H pointing toward the tringular face of Ar_3 and one face of the Ar_4 tetrahedron, respectively. Electrostatic modeling of intermolecular potentials has recently been extensively reviewed.[24]

B. The Role of *ab Initio* Calculations

Ab initio electronic structure calculations are playing an increasingly important role in the advancement of our knowledge of intermolecular interactions. The ability to arbitrarily sample any region of the intermolecular potential surface provides capabilities not easily obtained from experiment, although as we have noted above, accurate experimental potentials now exist for a few simple systems over a wide range of monomer orientations.[22,175,179–181,259]

The choice of basis functions and level and manner of treatment of electron correlation is a subject of considerable examination. The supermolecule calculation, correcting basis set superposition error by the Boys counterpoise procedure, is becoming relatively widespread. With the commercial availability of effective electron structure computation packages and quite adequate computer work stations, an increasing number of virtually whole potentials now exist. For Ar_2, about 95% of the well depth is obtained with large spdfgh type basis and either MP4 or CCSD(T) level of theory. A large basis calculation of $(H_2O)_2$ at a single nuclear configuration indicates that correlation accounts for about 40% of the binding energy, D_0. It is not obvious, however, whether the basis sets and levels of theory employed to model these system will be the most suitable for the more strongly bound van der Waals complexes.

A promising method which keeps the size of the basis set manageable uses midbond functions.[278] This procedure appears to be especially useful for the anisotropy. Global potentials including the dependence upon H—F bond length have been produced for Ar–HF,[279,280] Ar–H_2O,[280] and Ar–NH_3[280] which are in very good accord with the above described semiempirical potentials. The attractiveness of perturbation methods is somewhat mitigated by the complexity induced by the electron antisymmetry requirement.[281] However, the apparent physical clarity of the individual energy contributions is likely to produce demands for an increase in this form of presentation.

It is not surprising that dimers of the first row hydrides, with their relatively small number of electrons, have attracted a significant amount of the attention among quantum chemists.[282] Indeed, the dimers of two of the first row hydrides, H_2O and HF, have served as model systems for the development and testing of *ab initio* methods for studying hydrogen bonding while the dimer of BH_3 has given rise to the concept of a bridged hydrogen bond. The most extensive calculations have been undertaken on $(H_2O)_2$[283] and $(HF)_2$.[55] The calculations have met with considerable success at reproducing the experimental geometry and the qualitative features of the tunneling dynamics in these systems and hence led to the expectation that *ab initio* methods would be able to explain the rather surprising non-hydrogen bonded structure for the related first row hydride dimer, $(NH_3)_2$.[91–93] This has turned out not to be the case, however. Similar approaches applied to $(NH_3)_2$ have led to a variety of geometries, and have raised questions about the correctness of the theoretical and experimental geometries.[284] Until recently, *ab initio* calculations[285–293] almost universally gave a hydrogen bonded structure for this sytem, in which a hydrogen of one NH_3 unit was directed toward the lone-pair orbital of the other, analogous to the structures found for $(H_2O)_2$,[283] $(H_2O)_3$,[283] and $(HF)_2$.[55] Indeed, the problems surrounding $(NH_3)_2$ will need to be addressed in order to have confidence in the application of *ab initio* methods to more complex interactions such as those found in biological systems.

It has been discussed[262] that the origin of the incorrect geometry in $(NH_3)_2$ is due to the more rapid convergence of the dispersion energy for configurations in which a hydrogen, with its bond function, is located between the nitrogens. Configurations near the C_{2h} geometry with standard atom center basis functions are not as converged in the dispersion energy. Large basis set correlated calculations which supplement the typical atom centered basis set with bond functions between the nitrogen nuclei give a C_{2h} geometry for the dimer.[262] Giving further confidence to this approach is the ability of these types of calculations to reproduce accurately many of the features of the experimental Ar−HF, Ar−H_2O, and Ar−NH_3 pair potentials.[294]

The origin of an electric dipole moment in the observed "C_{2h}" $(NH_3)_2$ rotational spectrum[91−93] is assumed to be due to the fact that the observed states arise from two inequivalent NH_3 units, differing in nuclear spin and in angular momentum about the 3-fold axis.[262] More recent Stark effect measurements[99] reveal very small dipole moments for states in which the two tops have the same degree of internal excitation. Verification of these results will require calculating a complete potential surfaces for the C_{2h} dimer and modeling of the dynamics on the surface to calculate electric dipole and nuclear quadrupole hyperfine constants. Such an approach has been undertaken on an *ab initio* potential which gives a hydrogen bonded minimum for the dimer.[96] Multidimensional nuclear dynamics calculations for several potential surfaces have been made.[295] They presently indicate a preference for a hydrogen bonded minimum energy configuration with very small interchange barrier. Since explicit distance dependence of the potential anisotropy is important, however, it is likely that this problem will remain active and argumentative for some time.

C. When Do Experiments Become Unnecessary?

As *ab initio* calculations improve in accuracy with increased computational power, it is expected that in the future many of the questions now being addressed experimentally will be more efficiently attacked by theory. It is becoming clear, for instance, for the more strongly bound complexes, that *ab initio* theory can predict the minimum energy geometries accurately. In some sense, this has made qualitative features of geometry a less important issue experimentally. However, as the systems become less anisotropic and more weakly bound, such as in $(NH_3)_2$, the results of *ab initio* calculations are not viewed as reliably. As $(NH_3)_2$ has shown us, the problem often breaks down to how to make the comparison between theory and experiment in the face of complications posed by the large-amplitude motions. Thus, at least for a while, limiting the utility of the *ab initio* calculations for moderately complex systems will be the difficulty of doing the dynamical modeling on the surfaces. Increasingly in the future, more effort will be required to understand the vibrational problem to allow for meaningful comparisons to be made between experiment and *ab initio* theory.

V. Chemistry through Clusters

An interesting application of high-resolution work on weakly bound systems has involved the study of species which correspond to intermediate stages in "chemical" transformations. In some cases, these have been species with only one important minimum in the potential energy surface, but whose bonding is, by some criterion, intermediate between van der Waals and ionic or covalent. In other cases, they are species trapped in a high-energy local minimum along the reaction path for some chemical process and *are* themselves reactive intermediates. In either case, such species have become experimentally accessible and their study has offered some interesting new perspectives on chemistry and bonding.

A. Weak Bonding vs Chemical Interactions

In principle, there is nothing to prohibit a continuous transition from van der Waals to covalent or ionic bonding. Yet the majority of common interactions fall more-or-less into these two broad categories. Over two decades ago, however, it was recognized that a continuous range of behavior between the chemical and nonchemical limits can indeed be realized in crystals. Bent, for example, collected crystallographic data and showed that, depending on the compound, the distances between the same two atoms could vary almost continuously between those expected for van der Waals and covalent interactions.[296] In the crystalline adducts of I_2 with dithiane, tetrahydroselenophene, and di-*p*-dichlorophenyltellurium iodide, for example, the I−I bond lengths varied from 2.79 to 2.91 to 3.85 Å, respectively, a range bracketed by the 2.67 Å bond length in free I_2 and the 4.30 Å sum of the iodine van der Waals radii. Analogous variations in bond angles were ubiquitous.

More recently, Legon and co-workers have used the pulsed nozzle Fourier transform microwave technique to examine proton transfer in series of *gas phase* complexes of the form R_3N−HX. Since the proton is generally hard to locate, the degree of proton transfer was assessed not structurally, but rather by examination of intermolecular stretching force constants and nitrogen and halogen nuclear quadrupole coupling constants. In H_3N−HCl[297] for instance, both the force constant and the ^{35}Cl quadrupole coupling constants are significantly closer to those observed in the hydrogen bonded complex HCN−HCl than to those in the gas phase ion pair Na^+Cl^-. Indeed, the force constant is commensurate with that expected for a weakly bound complex, and the ^{35}Cl quadrupole coupling constant can be reasonably well calculated using *ab initio* response tensors for the HCl, and a distributed multipole description of the NH_3. Methylation of the ammonia, however, which makes the amine a better electron pair donor, produces observable progress toward the ionic limit. Thus, in $(CH_3)_3N$−HCl, eqQ(^{35}Cl) is significantly closer to that in Na^+Cl^- than in HCN−HCl, and the stretching force constant is 4 times larger than that predicted for a weakly bound system.[298] It is clear, then, that the ionic form $(CH_3)_3NH^+Cl^-$ must be an important part of the description of the complex, although a quantitative assessment of the degree of ionic character has not yet been possible. Similarly, in the series $(CH_3)_3N-HX$ (X = F,[299] Cl,[298] Br,[300] I[301]), the proton affinity of the halogen decreases going down the periodic table, and the degree of ionic character of the complex correspondingly increases. Here, crude estimates of the percent proton transfer can be made from the quadrupole coupling constants, and the results, using the halogen coupling constants, indicate a steady increase from 62% in the HCl complex to 93% in the HI complex! The fascinating work on these and related systems has been reviewed in great detail elsewhere.[23b]

The intermediate regime between van der Waals and *covalent* bonding has recently been investigated by Dvorak et al.[302] and Reeve et al.[303] in microwave spectroscopic studies of the donor–acceptor adducts CH_3CN-BF_3 and $HCN-BF_3$. The observed B–N bond lengths in these species are 2.011(7) and 2.47(3) Å, respectively, and sharply differ from the limiting van der Waals and covalent bond B–N bond lengths of 2.88 and 1.64 Å, respectively. Moreover, in CH_3CN-BF_3, the out-of-plane deformation of the BF_3 is 5.6(6)°, while the corresponding change in the HCN complex is between 0 and 3°. Clearly, from a structural standpoint, these complexes lie between the weakly bound and covalent limits. Interestingly, however, despite the 0.46 Å difference in bond lengths, the stretching force constants are equal to within 10%, and both values are well within the range characteristic of truly weakly bound systems. The calculated binding energies are 24[304a] and 22 kJ/mol[304b] for the CH_3CN and HCN adducts, respectively, and are also nearly equal, yet they are slightly stronger than that for a typical van der Waals interaction such as that in $NCCN-BF_3$, whose binding energy is only 13 kJ/mol.[303a] The quadrupole coupling constant of the boron in the HCN complex is virtually identical to that in the weakly bound species $Ar-BF_3$,[305] but that for the CH_3CN adduct is measurably less. It is clear from these results that different physical properties evolve at significantly different rates as a van der Waals bond is transformed into a chemical bond.[303]

Another species of interest along these lines is the complex SiF_4-NH_3[306] which has also been observed by pulsed nozzle FT microwave spectroscopy.[306a] Here, the $F_{axial}-Si-F_{equatorial}$ angle is distorted by 12° from the tetrahedral angle, and the dipole moment of the complex is enhanced by $1.381(3) \times 10^{-29}$ Cm (4.14(1) D) over the sum of the monomer moments! *Ab initio* calculations[306b] place the binding energy at 43.9 kJ/mol, making the interaction stronger than a van der Walls bond, but weaker than a normal chemical bond. The origin of the dipole moment enhancement has been investigated[307] and appears to be due to the geometric distortion of the SiF_4 and the large polarity of the (predominantly ionic) Si–F bond.

B. New Connections to Crystallography

Normally, crystallization of a system of isolated, gas phase molecules produces little discernable change in intramolecular bond lengths and bond angles. Typical gas–solid structure differences are on the order of 0.01 Å for bond lengths and 0.1° for angles.[308] For particularly weak bonds, however, this is not necessarily the case, as clearly demonstrated by the CH_3CN and HCN adducts of BF_3, described above. Both CH_3CN-BF_3 and $HCN-BF_3$ form molecular crystals, and a remarkable feature of these systems is that they exhibit enormous differences in structure between the gas phase and solid state. The formation of the molecular crystal of CH_3CN-BF_3, for example, is accompanied by a 0.381(11) Å contraction of the BN bond, and a 10° widening of the NBF angle. Although the complex is the intermediate type in the vapor phase, the crystal is comprised of covalently bonded units with a 1.630(4) Å B–N bond distance and a tetrahedral geometry at the boron. A recent crystallographic study of $HCN-BF_3$[309] has shown a similar structure and, since the gas phase bond length is significantly longer than that in the acetonitrile complex, the shortening of the bond upon crystallization is 0.835(31) Å! These are enormous effects by any measure and it is likely that they are closely connected with the "intermediate" nature of the gas phase bonds. Due to the electron deficiency of the boron in BF_3, the systems have a built in propensity to form new bonds, and the degree to which this occurs may be tuned either chemically or environmentally. In the latter case, the act of assembling the crystal lattice in effect drives the formation of covalent bonds, quite possibly by cooperative electrostatic effects and/or the added compactness associated with smaller subunits.

While the gas–solid structure differences of the BF_3 adducts are particularly dramatic, such effects are not entirely without precedent. An excellent example is the donor–acceptor adduct $(CH_3)_3N-SO_2$, whose gas phase and solid state crystal structures have been determined by Kuczkowski and co-workers.[310] The N–S bond length in the gas phase was found to be 0.21 Å larger than that in crystal, again indicating a significant environmental perturbation on an intramolecular bond. By using *ab initio* calculations and the known X-ray crystal structure, it was shown that the combination of a relatively flat potential minimum and a sharply rising dipole moment function could allow the total added dipolar interaction energy in the solid to exceed the energetic cost of contracting the N–S bond. Although the authors commented that the calculations were only approximate, the qualitative agreement with experiment nicely showed the feasibility of such a mechanism, at least in that case. Further calculations for this system have indicated that the enthalpy of formation is 44.8 kJ/mol and that the N–S bond has a significant ionic component.[311]

C. "Reaction Paths" from Complexes

The ability to observe interactions which vary between the van der Waals and covalent limits permits a new twist on the study of chemical reaction dynamics. Following Bent's observation of the wide variations in bonding in crystalline systems, Bürgi and Dunitz and co-workers introduced the so-called "structure correlation" method for following the

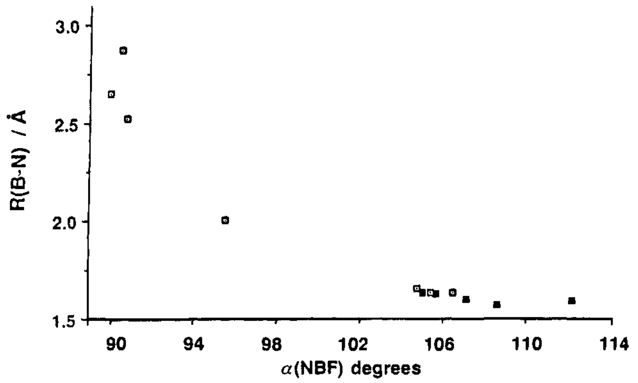


Figure 4. A plot of the B—N bond length vs the N—B—F (or N—B—H) angle for the addition complexes of BF_3 and BH_3 with nitrogen donors. Open squares represent gas phase data, and solid squares correspond to crystallographic results. (Reprinted from 302. Copyright 1992 American Chemical Society.)

changes which occur during the course of a chemical reaction.[312] The idea was that within a series of related crystalline compounds, key structural parameters (e.g., bond lengths and/or angles) could be identified, and their continuous, correlated variations (when observed), could be interpreted as a depiction of the reaction path for some simple chemical transformation. Interestingly, one of the early examples of this so-called "structure correlation method" involved the hydrogen bond. Using results from neutron diffraction studies on series of crystals containing collinear or nearly collinear hydrogen bonds, the O—H bond lengths in the O_1—H- - -O_2 moiety were found to vary from roughly 0.9 to >2 Å. The systematic correlation between the O_1—H and H—O_2 bond lengths was interpreted as a glimpse of the reaction path for proton transfer. These types of studies have been widely applied to crystalline systems, giving "reaction paths" which are generally consistent with chemical intuition.[312]

Figure 4 shows an analogous plot for BF_3 systems with nitrogen donors, and it is clear that the distortion angle of BF_3 is well correlated with the B—N distance. Thus, by borrowing established ideas from the solid state, the plot may be interpreted as a depiction of the reaction path for the formation of a B—N bond. If such an interpretation is correct, one can infer, for example, that when the nitrogen donor has reached half-way between the van der Waals and covalent bond distances, the BF_3 has distorted only about 5°. Stated differently, most of the electronic reorganization at the boron which accompanies the formation of the dative bond does so in the second half (last 0.5 Å) of the approach. We note that underlying this method of mapping reaction paths is the assumption that the progression of structures corresponding to a series of related but distinct compounds does indeed correspond to the changes which take place when a *particular* compound forms. A critical test of this assumption has not been possible for the crystal phase data, since the molecules involved have generally been quite complex. These simple gas phase systems, however, are particularly amenable to *ab initio* calculations of the reaction path, and the necessary comparison has thus become feasible. Calculations of the reactions paths for the BF_3 + NH_3 and BF_3 + HCN systems are currently in progress.[313]

D. Observation of Real Chemical Intermediates

Other studies have focused directly on the observation of complexes which act as intermediate stages in more complex chemical transformations. Perhaps the best example involves the ozonolysis of ethylene. This reaction has been well studied in both the gas and solution phase[314] and appears to proceed via the initial 1,3-dipolar cycloaddition of the ozone across the double bond to form a "primary ozonide". This species is unstable and undergoes a cycloreversion reaction to give an aldehyde, and the so-called "Criegee intermediate", $>C^+—O—O^-$, which then recombine to form a secondary ozonide. The structures of the ozonides appear previously to have been derived largely by inference from a variety of chemical and spectroscopic data, but the primary ozonide has recently been thoroughly characterized by rotational spectroscopy.[315] By allowing ozone and ethylene to co-condense and then warm in a waveguide cell, Gillies et al. were able to observe the unstable primary ozonide by microwave and millimeter wave spectroscopy. An impressive characterization of the lowest energy conformation was possible, as was a measurement of the dipole moment and an estimate of the barrier to pseudorotation (ring twisting). The use of deuterium substituted ethylene demonstrated the stereospecificity of the addition of O_3 to the double bond.

The *weakly bound complex* between ozone and ethylene was later investigated by the same group.[316] This time, using pulsed nozzle FT microwave spectroscopy, a shallow van der Waals minimum in the reaction path, occurring prior to the formation of the primary ozonide, was characterized. The complex has C_s symmetry with the planes of the ozone and the ethylene nearly parallel and an internal motion corresponding, at least in part, to 180° rotation of the C_2H_4 about its C_2 axis perpendicular to its plane. The observed structure, which corresponds to a π-type complex, is stereochemically quite similar to the transition state leading to the primary ozonide, and suggests that the nature of the van der Waals species can exert significant influence on the stereochemical outcome of the reaction. It is interesting to note how, although electrostatic pictures of weak interactions have largely overtaken the older HOMO—LUMO picture, the latter reenters the description as the bridge to chemical interactions is made. Figure 5 shows the detailed structural information about the course of ozonide formation which is now available from microwave spectroscopy.

A variety of other systems have been examined which are essentially van der Waals in character, but which are formed between molecules which normally react under bulk conditions. Only by virtue of short mixing times and the collision-free environment of the supersonic jet can these species be isolated. The ammonium halides and the BF_3 adducts are, of course, similar in this sense, but the chemistry of the "real chemical intermediates" is not as simple, and cannot be reversed by "evaporation". Examples of systems of this type are $H_3P—Cl_2$,[317] $CH_3NC—HX$ (X

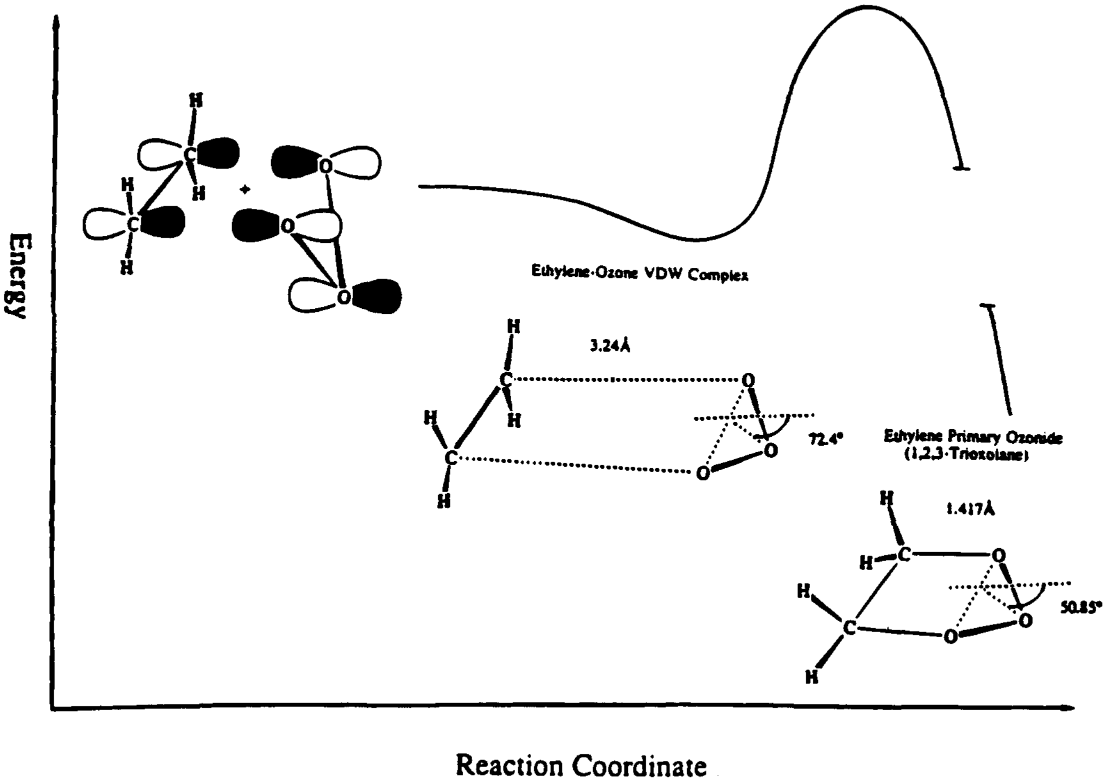


Figure 5. Illustration of structures at various points along the reaction path for the ozonolysis of ethylene. (Reprinted from 316a. Copyright 1991 American Chemical Society.)

= F, Cl),[318,319] and $(CH_2)_2O-HCl$.[320] Phosphine, for example, reacts violently with Cl_2 to form $H_2PCl + HCl$. One possible mechanism involves, first, the formation of an H_3P-Cl_2 adduct, followed by charge transfer to form an $[H_3PCl]^+Cl^-$ intermediate, which subsequently eliminates HCl. The primary van der Waals adduct, has been observed,[317] but the charge transfer adduct itself remains undetected in the gas phase. Whether it exists without the benefit of solvent stabilization, of course, is an open question.[317]

VI. Conclusion

Two decades ago, when the first microwave spectra of weakly bound complexes were obtained, it was hard to predict the scope of the field which was to grow out of these measurements. Many goals were set: Understanding the origins of intermolecular forces at a modern level, making the extension to many-body interactions and condensed phase systems, and meeting the clear need to develop formalisms for treating the multicoordinate large amplitude vibration problem. The study of infrared and optical photodissociation introduced an irreversible link to chemical dynamics, and many questions about predissociation rates and the dependence of the interactions on monomer excitation arose. Today, it is quite pleasing to see that so much of the effort spent toward meeting these early goals is actually coming to fruition. The ability to extract accurate potentials from spectroscopic data has been clearly demonstrated, and the complexity of systems which are tractable is growing rapidly. With it, the ability to make concrete statements about many-body interactions is finally possible. Predictive methods are becoming increasingly routine, and it is not too unreasonable to hope that they may be soon be able to replace some experiments at a reasonable level of accuracy. Finally, the use of experimental and theoretical tools developed for studying weakly bound systems is finding application in elucidating at a new level of detail the molecular processes involved in chemical reactions. All in all, the study of weakly bound systems has been an exciting endeavor and is likely to remain one for some time to come!

VII. References

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