FEATURE ARTICLE

Vibration–Rotation–Tunneling Spectroscopy of the van der Waals Bond: A New Look at Intermolecular Forces

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Measurements of the low-frequency van der Waals vibrations in weakly bound complexes by high-resolution laser spectroscopy provide a means to probe intermolecular forces at unprecedented levels of detail and precision. Several new methods are presently being used to record vibration–rotation–tunneling (VRT) transitions associated with the motions of the weak bonds in van der Waals clusters. The most direct measurements are those probing only the van der Waals modes themselves, which occur at far-infrared wavelengths. This article presents a review of the information on both intermolecular forces and intramolecular dynamics that has been obtained from far-infrared VRT spectra of 18 complexes during the past several years. Some rotationally resolved measurements of van der Waals modes observed in combination with electronic or vibrational excitation are also discussed.

Introduction

Molecular descriptions of condensed matter depend on having a knowledge of the pairwise interactions as well as the many-body forces which govern the dynamics of discrete constituents. By modeling the microscopic behavior of bulk phases, scientists can elucidate the basic physics underlying such diverse phenomena as solubilities, phase transitions, micelle formation, protein folding, friction at the solid–solid interface, and electron transport in solution. Modern formulations of the many-body dynamics in such problems (e.g., simulated annealing, Monte Carlo sampling, molecular mechanics) now influence a very large number of scientists, as new generations of supercomputers become increasingly more accessible. Interestingly, the mathematical representations of intermolecular forces which constitute the input to these models remain remarkably primitive. Even the most sophisticated calculations of this type employ severe approximations to the inter- and the intramolecular forces. Some of the most widely used potentials compress the combined effects of pairwise and many-body forces into effective pair potentials experienced by an individual molecule. Such effective potentials do allow approximate description of the collective behavior of the molecules in the condensed phase, but by construction, they are incapable of describing the behavior of the individual molecules. Moreover, they are generally incapable of providing a physically relevant description of related phenomena which depend on the specific properties of the individual molecules.

Experimental efforts to study intermolecular forces, and to thereby provide accurate intermolecular potential energy surfaces (IPS) for pairwise and many-body interactions, have a long history. Properties of liquids and solids which depend strongly on the details of intermolecular forces (phase diagrams, diffusion coefficients, and pressure broadening) are of interest to a broad range of problems. Early experiments measuring gas-phase nonidealities, e.g., second virial coefficients, diffusion coefficients, and pressure broadening cross sections for vibrational and rotational spectra, reduced the complexity of the problem to that of understanding the pairwise interaction between two particles. These represented the initial attempts of experimentalists to establish control over the number of degrees of freedom which the molecules sample during the measurement. Many-body forces are discriminated against in these experiments by reducing the number density of the molecules sufficiently to keep the frequency of ternary and higher order collisions negligible. However, results from these collisional experiments still represent an average over a thermal distribution of collisional energies, as well as over the relative orientation and the impact parameter of the colliding pair. This is still an overwhelming number of degrees of freedom, unfortunately precluding the elucidation of accurate IPS's from even these simpler types of data.

Results from such experiments traditionally have been interpreted in terms of an orientationally averaged effective isotropic pair potential. However, isotropic potentials are far too simplistic to provide a basis for understanding the molecular dynamics of bulk material, as the anisotropy (orientational dependence) is a dominant feature in most condensed-phase systems. For example, hydrogen bonding, a common terminology for describing the

strongest attractive anisotropy in pairwise intermolecular forces, is well-known to chemists and biologists, for its manifestations are both endemic and dramatic. Ternary dispersion forces between atoms are thought to be dominated by the Axilrod-Trotter intermolecular, an anisotropic three-body force. Anisotropic repulsive forces account for the effective shapes of molecules and constitute the dominant anisotropic contributions in several contexts, although they are the least well understood of the principal anisotropic forces. Anisotropic attractive forces include electrostatic, induction, and dispersion interactions. There is a considerable body of theoretical studies of the appropriate functional forms for these interactions, although to date these have not been thoroughly tested.

Experimentalists, frustrated with the level of detail provided by bulk collisional measurements, attempted to implement additional control over the conditions of the collisional event. Molecular beam scattering experiments provide a substantial degree of such control, not only reducing the number of particles involved to two but also accurately characterizing their relative velocity. These experiments are most sensitive to the anisotropy in the repulsive region of the IPS, but they may, in principle, be used to determine a global anisotropic IPS. (We use the term global to mean over the full range of intermolecular coordinates, not over the full range of inter- and intramolecular coordinates, as is sometimes implied.) In practice, however, it has not been possible to determine a global IPS from scattering data except in the most favorable cases, such as Ne–H₂.¹⁰ as the energy resolution of these experiments is usually inadequate for the task. Characterizations of the anisotropy in several other systems containing H₂ or He have recently been obtained from state of the art scattering experiments.

High-resolution spectroscopy of clusters formed from the components whose interaction potential is of interest offers the prospect of obtaining the ultimate possible control with respect to averaging over the IPS. Unlike bulk collisional and molecular beam scattering experiments, which necessarily involve averaging over both a distribution of collisional energies and an extensive range of intermolecular separations and orientations, high-resolution spectroscopy probes essentially monoenergetic, well-defined eigenstates of the system. Thus, the intermolecular potential can, in principle, be probed at an extraordinary level of detail by measuring the properties of different eigenstates, each of which samples a distinct region of the IPS. An additional advantage of high-resolution spectroscopy is that it can be adapted for the study of noncovalent interactions easily; magnetic resonance techniques, since the observed spectra can be more straightforwardly assigned to a particular cluster size.

Application of high-resolution spectroscopy to the study of molecular clusters began in 1971 with the work of McKellar and Welsh,¹² who obtained rotationally resolved spectra of rare gas (Rg)–H₂ clusters in the near-infrared region. Subsequently, the powerful techniques of microwave spectroscopy were employed for this purpose by Klempner and co-workers,¹³ who developed the molecular beam electric resonance (MBER) method for the study of superpositionally generated clusters. Rotational constants, tunneling frequencies, dipole moments, and quadrupole hyperfine coupling constants have now been measured for over 100 complexes using this technique and the Fourier transform microwave spectroscopy method subsequently introduced by Balle and Flygare.¹⁴ These microwave studies provide a highly accurate probe of the region of the IPS sampled by the ground intermolecular vibrational state of the complex. A summary of these results has been presented by Novick.¹⁵ Experimental electronic spectra of complexes also typically sample the IPS near the van der Waals minimum in both the ground and excited vibronic state. Extraction of the anisotropic IPS from these experiments alone has proven to be nearly impossible, although IPS's for Ne–HCl¹⁶ and Ar–HBr¹⁷ have actually been extracted from microwave spectra alone. For most systems, however, even in combination with collisional measurements of the type discussed above, the information provided by microwave spectroscopy and electronic spectroscopy of clusters is still inadequate: the ground intermolecular vibrational state simply does not sample a sufficiently extensive region of the IPS to permit its characterization.

This constraint applies as well to infrared spectra of the intramolecular modes of the constituent monomers of a cluster. Because of the large separation in time scales between intramolecular vibrations (1000–4000 cm⁻¹) and intermolecular vibrations (10–400 cm⁻¹), the intramolecular modes can be treated as adiabatically separable from the intermolecular modes, much as electronic motion is separated from vibrational motion in the Born–Oppenheimer approximation. A different IPS is thus obtained for each vibrational level of the monomers, and probes of the vibrationally excited IPS therefore rely on the detection of hot bands and combination bands. This capability has recently been demonstrated in an impressive fashion by Nesbitt and co-workers.¹⁸ Rotationally resolved infrared spectra of complexes can now be obtained using a number of modern techniques. In many cases, vibrational predissociation has also been observed, providing interesting new insight into the coupling between the ground- and excited-state potentials. The recent reviews of Nesbitt¹⁹ and Miller²⁰ provide excellent guides to this literature.

In addition to the difficulty of obtaining precise and detailed experimental probes of the intermolecular potential, computational methods for accurately treating many-body dynamics have been either too costly or intractable given the available theoretical techniques and computers. Such calculations are essential for assessing whether a given mathematical form of the IPS adequately represents the physics of the interaction. Accurate calculations of the eigenvalues and eigenvectors, or of collisional averages over the IPS, require explicit treatment of all of the degrees of freedom simultaneously. Approximations which reduce the dimensionality of the calculations in an effort to make them tractable are often too rough that one misses the essential features of a trial IPS. Over the past several years, dramatic progress in theoretical approaches to calculating the spectra of weakly bound (and highly vibrationally excited) molecules and the increasing availability of modern supercomputers have allowed the accurate computation of the eigenvalues and eigenvectors of multidimensional systems, as well as the detailed calculation of some collisionally averaged properties on multidimensional anisotropic IPS's. These developments are discussed in recent reviews by Cohen and Saykally²¹ and by Light et al.²² and in the papers by Green et al.²³,²⁴ Hutson's discussion of approximate methods for treating the intermolecular dynamics of atom–molecule clusters provides an excellent introduction to the theoretical treatment of cluster eigenstates and their dynamics.²⁵

These theoretical advances have been paralleled by the development of new direct spectroscopic probes of the intermolecular dynamics of weakly bound complexes. Such spectra provide the ideal route to specific information about regions of the IPS displaced from the global minimum. We call such approaches vibration–rotation–tunneling (VRT) spectroscopy to emphasize that the measured spectra typically sample regions both above and below the barriers to internal motion on the IPS. As a result, terminologies associated with conventional notions of vibrational spectroscopy, or with the study of low-frequency tunneling motions, are often equally appropriate.

Solvated molecules are usually present in their ground vibrational levels, imparting a special importance to the measurement of the IPS for the vibrational ground state of the monomers; viz., it is this ground-state surface which usually governs the structural and dynamical behavior of bulk fluids and molecular solids. Determination of the ground-state IPS requires direct access to the internal vibrational modes of the cluster, which occur at frequencies from 10 to 500 cm$^{-1}$, i.e., in the far-infrared (FIR) region. The FIR has been one of the technologically most difficult regions of the electromagnetic spectrum to access. This region has been largely ignored, as developments in microwave technology and near-infrared laser sources have made high-resolution spectroscopy in these adjacent regions relatively routine. Practical tunable lasers in the FIR region have become available only quite recently. In the following pages, we review the development of VRT spectroscopy, focusing on the application of tunable far-infrared laser and Fourier transform FIR spectroscopy for direct measurement of van der Waals vibrations. Some references to rotationally resolved IR, visible, and UV spectra of van der Waals vibrations involving intramolecular excitation will be included whenever a comparison of the spectra is warranted, but no attempt is made to present a comprehensive review of these studies here, as this has been provided elsewhere.\(^{(1,19)}\)

**Ar–HCl: A Prototype for Intermolecular Potential Surfaces and VRT Dynamics**

A decade ago, Hutson and Howard determined two intermolecular potentials for the Ar–HCl system.\(^{(25)}\) Both of the potentials were extracted from the best available experimental data, including microwave rotational spectroscopy in the ground state of the cluster, molecular beam scattering, and pressure broadening of HCl rotational lines by argon. One surface (M3) had a single prominent minimum in the linear Ar–HCl configuration, while the second (M5) exhibited a substantial secondary minimum at the linear Ar–CH\(_2\)H geometry. The experiments that were technologically feasible at the time were incapable of discriminating between these two very different topologies, but it was suggested that direct measurement of VRT spectra could distinguish between them.

High-resolution laser measurements of VRT spectra for Ar–HCl were first performed in 1983 by Howard and Pine,\(^{(26)}\) who measured the $\Pi(\jmath=1)$ bending vibration of the cluster in combination with $\nu = 1$ of the HCl stretch, and by Marshall et al.,\(^{(27)}\) who measured the $\Pi(\jmath=1)$ fundamental vibration directly in the FIR region (near 34 cm$^{-1}$) with resolution of both rotational and nuclear quantum number. These studies signaled the beginnings of a new era in the study of intermolecular forces. The infrared measurements were obtained using a tunable difference frequency laser to measure the absorption by clusters produced in a cooled multipass cell. In the FIR measurements, an electric field was used to tune the cluster resonances from their zero-field frequencies into coincidence with an available fixed-frequency FIR laser line. Molecules which absorbed the FIR light were subsequently extended by Ray et al.,\(^{(28)}\) who developed a much more sensitive electric resonance approach. By generating the cluster beam inside the cavity of a FIR laser, Ray et al. took advantage of the increased path length from multipassing of the FIR laser beam, the enhanced sensitivity of the output power to losses (absorption) in the cavity due to nonlinear response of the gain medium, and the higher densities of clusters which could be used in an unskimmed supersonic beam. Using this technique, termed "intracavity FIR laser electric resonance spectroscopy", the measurements of three of the lowest vibrational levels of Ar–HCl—the $\Pi(\jmath=1)$ bend (34 cm$^{-1}$), the $\Sigma(\jmath=1)$ bend (24 cm$^{-1}$), and the intermolecular stretching vibration (32 cm$^{-1}$)—were completed by Robinson et al.\(^{(30)}\) This data set proved sufficient to unambiguously conclude that the IPS for Ar–HCl possesses a double minimum, answering the lingering question that was raised by Hutson and Howard 10 years before.\(^{(31)}\) Hutson\(^{(32)}\) subsequently fit the new FIR–VRT data and a measurement of the binding energy obtained from infrared vibrational predissociation measurements by Howard and Pine to an anisotropic IPS, denoted H6(3). The spectroscopic efforts leading to the development of the H6(3) surface have been reviewed by Saykally.\(^{(33)}\)

Ar–HCl has become the prototype for understanding intermolecular forces and VRT dynamics in 2-dimensional systems with moderate anisotropy. Systems with very weak anisotropy are better compared with the Rg–H\(_2\) systems, which have been studied in the near-infrared region.\(^{(12,23)}\) Anticipating the subsequent content of this review, a consideration of the dynamics of the VRT levels of Ar–HCl is highly instructive. We begin by constructing a basis consisting of the free rotor wave functions of the HCl monomer and a series of stretching eigenfunctions from a suitable 6–12 potential. In this basis, the first two excited bending vibrations are labeled $\Sigma(\jmath=1)$ and $\Pi(\jmath=1)$, where the letters $\Sigma$ and $\Pi$ denote levels that correlate to $m_\jmath = 0$ and $m_\jmath = \pm 1$ of the free rotor wave function, respectively. The isotropy of space is broken by the presence of the argon, and the $m_\jmath$ components of the $j = 1$ free rotational state of HCl become quantized along the $x$ axis of the cluster. Since Ar–HCl is the first system for which extensive VRT measurements were obtained, a variety of different labeling schemes for the VRT states has been used. Much of the literature on Ar–HCl and related systems is written in terms of the standard linear triatomic notation (Ray et al.,) for the VRT states, where $n_\ell$ refers to the monomer stretch, $n_2$ the intermolecular bend, and $n_3$ the van der Waals stretch. This labeling system is not incorrect, but it conveys the idea that some of the usual rigid rotor–harmonic oscillator ideas are useful and appropriate for the description of the VRT states when, in fact, they are not.

The nature of the Ar–HCl IPS, as determined from the VRT spectroscopy, has been discussed by Hutson.\(^{(31,33)}\) Both of the relevant attractive forces, viz., induction and dispersion, favor the linear geometry in the orientation Ar–HCl but are essentially isotropic at other orientations, favoring neither the perpendicular geometry nor the inverted linear geometry Ar–CH\(_2\). The secondary minimum that is observed in the calculated linear geometry (Ar–CH\(_2\)) results from the weakening of the repulsive forces at this orientation. Hutson has rationalized this effect as resulting, in turn, from the electron-withdrawing effect of the hydrogen atom. This effect also explains the decrease in the difference in well depths between the primary and the secondary minimum found in the series Ar–HF (85 cm$^{-1}$),\(^{(34)}\) Ar–HCl


(35 cm\(^{-1}\)).\(^{31}\) Ar-HBr (5 cm\(^{-1}\))\(^{17}\) —the hydrogen withdraws less electron density from the highly electronegative F atom than it does from the much less electronegative and more polarizable Cl and Br atoms. From the Ar-HCl IPS and from subsequent studies of other systems, it has become apparent that the anisotropy of intermolecular forces results from the combination of both attractive and repulsive forces and that consideration of only the attractive forces is not sufficient if one is attempting to generate an approximate model for the IPS. The competition between attractive and repulsive forces is discussed in more detail later on with respect to its effect on the VRT dynamics of Ar-H\(_2\)O and Ar-NH\(_3\).

**Tunable Far-Infrared Laser Spectroscopy**

Only 2 years after the initial FIR-VRT spectroscopy studies of Ar–HCl, and while the measurements of the \(\Sigma\) bend and the intermolecular stretch were barely off to the publisher, Busarow et al.\(^{35}\) combined a versatile new tunable far-infrared laser system (Figure 1) with a CW planar supersonic expansion (Figure 2), which provided an exceptionally intense source of clusters. This combination has proven to be as sensitive as and much more complex systems can be expected in the near future, as more developed from these \(\Sigma\) bend and Ar–HBr.

**Figure 1.** Berkeley tunable far-infrared laser spectrometer.

**Figure 2.** CW planar supersonic jet design.

For the simplest clusters, the tunable far-infrared laser and the CW planar jet have been described in detail elsewhere;\(^{35,47}\) hence, only a brief overview

<table>
<thead>
<tr>
<th>cluster</th>
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<tbody>
<tr>
<td>Ar–H(_2)O</td>
<td>36–41</td>
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<tr>
<td>H(_2)O–N(_2)</td>
<td>42</td>
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<tr>
<td>H(_2)O–CO</td>
<td>43</td>
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<tr>
<td>H(_2)O–CH(_3)</td>
<td>44</td>
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<tr>
<td>H(_2)O–C(_2)H(_5)</td>
<td>45</td>
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<tr>
<td>NH(_3)–H(_2)O</td>
<td>46</td>
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<tr>
<td>(H(_2)O)(_2)</td>
<td>47–51</td>
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<tr>
<td>Ar–NH(_3)</td>
<td>51, 52–54</td>
</tr>
<tr>
<td>(NH(_3))(_2)</td>
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<tr>
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<td>57</td>
</tr>
<tr>
<td>Ar–HCl</td>
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<tr>
<td>Ar–HBr</td>
<td>60</td>
</tr>
<tr>
<td>Ar–HCN</td>
<td>61</td>
</tr>
<tr>
<td>Ar–HCl</td>
<td>62, 63</td>
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<tr>
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<td>64, 65</td>
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<tr>
<td>H(<em>2)C(</em>\equiv)N</td>
<td>66–69</td>
</tr>
<tr>
<td>HCN</td>
<td>70</td>
</tr>
<tr>
<td>HF–HCN</td>
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<tr>
<td>Rg–H(_2)</td>
<td>74</td>
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<tr>
<td>(H(_2)O)(_2)</td>
<td>75</td>
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</table>

the multidimensional intermolecular dynamics are developed. The tunable far-infrared laser and the CW planar jet have been described in detail elsewhere;\(^{35,47}\) hence, only a brief overview


42) Bumgarner, R. E.; Bowen, J.; Green, P. G.; Blake, G. A. Manuscript in preparation.


56) Loeser, J.; Saykally, R. J. Manuscript in preparation.


of these systems is given here. The tunable far-infrared (TFIR) laser was introduced independently by Bionic et al.\(^\text{78}\) and by Fetterman et al.\(^\text{79}\) in 1978. Significant improvements in the design of a FIR gas laser by Mansfield and co-workers\(^\text{80}\) led to the development of a much more powerful and general TFIR source by Farhoomand and Pickett.\(^\text{81}\) Also, the essence of the experiment, viz. the Schottky diodes which are used as the mixing device, has been fabricated with greatly improved conversion efficiency and operating bandwidth since the initial work TFIR lasers. The most recent advances in diode performance and design are described by Crowe et al.\(^\text{82}\) The current state of the art of TFIR laser technology is reviewed by Blake et al.\(^\text{83}\) The most important features of the currently used laser design are as follows; (1) high spectral resolution, ca. 10 kHz, which is significantly less than the few hundred kilohertz pressure and Doppler broadening obtained in the CW planar jet; (2) high sensitivity, fractional absorptions of 1 part in 10\(^6\) can routinely be measured; and (3) broad tunability in the range 300–3000 GHz (10–100 cm\(^{-1}\)) with some coverage at higher frequency.

The CW planar jet described by Busarow et al.\(^\text{35,76}\) is a conceptually simple design, requiring only a pair of carefully machined plates to form the planar orifice and to seal against the nozzle body and a high throughput pumping system. Planar expansions offer significant advantages relative to the more commonly used nozzle introduced by Nesbitt and Lovejoy,\(^\text{86}\) which does not require cooling of the mixing device, erasing some of the advantages of such a high throughput vacuum system, has also proven very successful. The powerful combination of a GaAs Schottky diode based TFIR laser and a CW planar jet is now employed by at least three research groups which are actively pursuing measurement of VRT spectra of van der Waals clusters. A fourth group, headed by Professor K. Leopold,\(^\text{60}\) is utilizing CW planar jet technology in combination with an alternative method for generation of TFIR radiation based on mixing CO\(_2\) radiation in a metal–insulator–metal (MIM) diode. Table I summarizes the ground-state VRT studies of complexes that have been made as of this writing, using tunable far-infrared laser spectroscopy and other techniques.

### Collisional Relaxation and Coordinate Systems of Clusters

Before turning to a discussion of the specific systems studied by VRT spectroscopy, it is useful to consider some general aspects of cluster formation in supersonic expansions and to specify a coordinate system for use in the subsequent discussions. The rates of cooling obtained in supersonic jets are not uniform for different degrees of freedom. It is well-known that the rapid cooling operative in a supersonic expansion allows bottlenecks in relaxation processes to create nonequilibrium distributions of population in the different VRT states of monomers and of clusters. While rotations are found to be nearly equilibrated with the low translational temperature of the beam, high-frequency monomer vibrational and rotational states are often frozen in at the room temperature thermal distribution. This was first shown by Becket al.\(^\text{37}\) for the benzene monomer and has since been discussed by Nelson et al.\(^\text{85}\) and by others with specific reference to molecular clusters. The nuclear spin bottleneck prevents relaxation of excited rotational states with different nuclear spin than the ground state from relaxing into that state, regardless of the energy difference. For example, even in 1 K beams, a substantial fraction of H\(_2\) molecules remain in the \(j = 1\) (ortho) rotational level although it is 60 cm\(^{-1}\) above the true \(j = 0\) ground state. Similarly, both ortho and para forms of H\(_2\) molecules are found with room temperature abundances in cold beams, although nearly 20 cm\(^{-1}\) separates the lowest ortho and para levels of these species. During an expansion, the different spin conformers of the monomers may associate to form distinguishable spin states of clusters. For instance, the H\(_2\)O dimer is formed in the para–para, para–ortho, ortho–para, and ortho–ortho.

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\(^{57}\) Cohen and Saykally

**Figure 3.** Jacobi coordinates for the interaction of two polyatomic molecules.
orthor-par, and ortho-ortho forms. Typically, these different forms are observed in the statistical ratios expected from the room temperature abundance of ortho and para molecules. This need not be the case, since the binding energy (thermodynamics) and the kinetics of formation and destruction of different spin conformers of a given cluster are not necessarily the same.

Throughout this work we choose to describe the complexes under study with a set of generalized Jacobi coordinates (scattering coordinates). The Jacobi coordinates appropriate for a complete description of the dynamics of any complex composed of two interacting polyatomic fragments in their ground vibronic states consist of five angles and a single distance. These are shown in Figure 3. The \( R \) vector joins the centers of mass of the two interacting monomers, pointing from molecule A toward molecule B, and defines the weak bond axis; \( \theta_1 \) and \( \theta_2 \) are the angles between \( R \) and an appropriate symmetry axis in each monomer, \( \phi_1 \) and \( \phi_2 \) describe rotation of each monomer about these symmetry axes relative to a well-defined reference orientation, and \( x \) is the dihedral angle between the symmetry axes. For complexes composed of atoms or linear molecules, some of these coordinates may be defined to be zero at all relative orientations. For trimeric and higher clusters, variations on this scheme will be employed.

\section*{H\textsubscript{2}O-Containing Clusters}

Weakly bound clusters containing the water molecule are of enormous interest because of the obvious importance of water in a wide array of contexts. It is therefore not surprising that the exact \( \text{H}_2\text{O}-\text{H}_2\text{O} \) pair potential and effective pair potential of water molecules in the bulk have been the subjects of literally thousands of studies. The IPS corresponding to water interacting with other molecules will also be useful in the development of a detailed understanding of intermolecular forces. For example, the intermolecular forces between water and nonpolar molecules are important in the famous "hydrophobic effect." The molecular interpretation of this phenomenon is the subject of continuing debate, which could perhaps be settled if the relevant IPS's were known precisely.

TFIR laser spectroscopy has been applied to several \( \text{H}_2\text{O} \)-containing systems. The simplest of these is the atom-molecule complex \( \text{Ar}-\text{H}_2\text{O} \), for which sufficient VRT spectra \cite{36,37,38} have been obtained to allow an accurate IPS to be generated exclusively from the spectroscopic data \cite{39}. The structurally more complex systems \( \text{N}_2-\text{H}_2\text{O} \), \( \text{CO-H}_2\text{O} \), \( \text{CH}_4-\text{H}_2\text{O} \), \( \text{C}_2\text{H}_6-\text{H}_2\text{O} \), \( \text{NH}_3-\text{H}_2\text{O} \), and \( \text{H}_2\text{O}-\text{H}_2\text{O} \) \cite{40,41,42} have also been studied by FIR-VRT spectroscopy, although not in such great detail.

In Figure 4, we show a correlation diagram depicting the relative energies of the VRT states associated with internal rotation of \( \text{H}_2\text{O} \) as a function of the magnitude of the anisotropy in the interaction potential. As the anisotropy is increased from zero (Figure 4a), the initial effect is the breaking of the \( (2j+1) \) spatial degeneracy of the free rotational energy levels of the monomer by the large internal fields present within the complex. This situation is depicted in Figure 4b and is pertinent for discussion of the \( \text{Ar}-\text{H}_2\text{O} \) complex, as well as for all other \( \text{H}_2\text{O} \)-containing complexes with moderate anisotropy. Additional increase in the anisotropy of the IPS causes substantial mixing of the different internal rotor levels \( j \), such that the internal rotor quantum numbers are no longer good labels for the states and a tunneling or vibrational language becomes more appropriate. One of the several possible energy level diagrams appropriate for the strongly anisotropic case is shown in Figure 4c.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Correlation diagram showing (a) free rotation, (b) weakly hindered internal rotation and (c) one possible near rigid limit for a complex containing \( \text{H}_2\text{O} \).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Computer-generated stick spectrum showing all nine bands of \( \text{Ar}-\text{H}_2\text{O} \) which have been observed by TFIR laser spectroscopy. The intensities assume a 5 \text{K} beam and normal relative intensities within each band. The different bands are scaled by the transition moments computed from a preliminary revision of the AW1 IPS (ref 91).}
\end{figure}

\section*{Ar-H\textsubscript{2}O: A Prototype for 3-Dimensional VRT Dynamics}

The most detailed VRT spectra among these clusters exist for \( \text{Ar}-\text{H}_2\text{O} \). The interaction of a nonpolar sphere, e.g., argon, with water has been considered to be a useful model of the forces associated with hydrophobic effects (see ref 37). This cluster is also a simple prototype for developing a detailed understanding of intermolecular forces in multimolecular complexes. It is the first system with more than two van der Waals degrees of freedom for which extensive VRT spectra have been obtained. These data have been used in the development of an accurate and detailed experimental IPS \cite{43,44}. The spectra indicate that \( \text{Ar}-\text{H}_2\text{O} \) has an equilibrium bond length of about 3.6 \AA \ and that the \( \text{H}_2\text{O} \) is nearly freely rotating within the complex.

Twelve lower VRT levels, corresponding to the \( \Sigma(0_{\text{II}}) \), the \( \Sigma \) and \( \Pi \) components of the \( (1_{\text{II}}) \), \( (1_{\text{II}}) \), \( (1_{\text{II}}) \), and \( (2_{\text{II}}) \) internal rotor states, the fundamental intermolecular stretch \( n = 1 \), \( \Sigma(0_{\text{II}}) \), and the stretching internal rotor combination levels \( n = 1 \), \( \Sigma(1_{\text{II}}) \) and \( n = 1 \), \( \Pi(1_{\text{II}}) \) of the normal isotope have been fully characterized \cite{36,37,38,39}. A calculated stick spectrum of all of the observed bands of \( \text{Ar}-\text{H}_2\text{O} \) is shown in Figure 5, and an energy level diagram for states bound by more than 30 \text{cm}^{-1} \ is shown in Figure 6. States with \( k_x = k_y = 0 \) are para and with \( k_x = k_y \) odd are ortho. Electric dipole selection rules permit only ortho-ortho and para-para transitions. The intermolecular vibrations are labeled by \( n \), the number of quanta of stretching excitation, which, for simplicity, we omit when \( n = 0 \); \( \Omega = \Sigma, \Pi, \Delta, \ldots \), the projection of the total angular momentum (and identically, the projection of internal angular momentum) on the pseudodiatomic axis; and \( j \), the free rotor level of the \( \text{H}_2\text{O} \) monomer to which the internal

\begin{itemize}
\item \cite{36,37,38,39,40,41,42}
\end{itemize}

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\item \cite{39}
\end{itemize}
Cohen and Saykally developed an adaptation of the collocation method, introduced for scattering and spectroscopic calculations by Yang and Peet, for the efficient calculation of the eigenvalues in 3-dimensional systems. This eigenvalue subroutine was then embedded in a least squares fitting routine and was used to fit the VRT data to a model IPS. The resulting IPS was denoted AW1. This fit provided the first unambiguous evidence of strong angular-radial coupling in this system. The orientation of the potential minimum on the AW1 surface is at $\theta = 55^\circ$, the linear hydrogen-bonded configuration, when the intermolecular separation is larger than $3.8 \text{ Å}$. At short intermolecular separations ($Q < 3.3 \text{ Å}$) the potential minimum on this IPS is at $\theta = 180^\circ$. This is a large change in the orientation of the potential minimum (angular-radial coupling), and it occurs precisely in the region of the IPS sampled by the first two radial wave functions. As a result, internal rotation and the van der Waals stretching motions are not even approximately separable. Strong angular-radial coupling had already been invoked in analysis by Cohen et al. of the effective radial potentials sampled by the different internal rotor levels of Ar-H$_2$O. However, the evidence was only an indication of the presence of angular-radial coupling and was not unequivocal. In the course of fitting the experimental data to a full 3-dimensional IPS, the energy of the $\Sigma(1_{11})$ state was observed to be strongly dependent on the anisotropy in the position of the radial minimum of the IPS. Calculations on the final IPS, denoted AW1, predicted that this state would be observed at different orientations about 100 GHz (3.3 cm$^{-1}$) above its companion the $\Pi(1_{11})$ state. This contradicts the predictions which are arrived at by assuming that all states sample the same effective radial surface. On Hutson's effective angular surfaces and on other more detailed purely angular surfaces which have been adjusted to reproduce some of the experimental data which have since been obtained, the $\Sigma(1_{11})$ state is always predicted to be below the $\Pi(1_{11})$ state. The 3-dimensional predictions thus provide an opportunity for testing the importance of angular-radial coupling in the IPS.

Direct measurements of FIR VRT transitions to the $\Sigma$ and $\Pi(1_{11})$, the $\Sigma$ and $\Pi(2_{12})$ internal rotor states, and the $n = 1$, $\Pi(1_{10})$ stretching-internal rotor combination state obtained since the development of the AW1 surface confirm the conjecture that angular-radial coupling in the IPS is large; in fact, the already substantial coupling in the AW1 surface was actually found to be too small. The $\Sigma(1_{11})$ band is measured to be 3.8 cm$^{-1}$ above $\Pi(1_{11})$, an additional 0.5 cm$^{-1}$ higher than the prediction. Analysis of the Coriolis effects in the $1_{11}$ internal rotor levels establishes that the $\Sigma(1_{11})$ eigenstate is a nearly 65:35 mixture of that basis state and the $n = 1$ $\Sigma(00)$ basis state with additional contribution from more highly excited states. Similarly, $\Sigma(2_{12})$ is shown to be very strongly mixed with $n = 2 \Sigma(00)$. Inspection of the wave functions obtained from full 3-dimensional quantum calculations using the collocation method confirms the conclusions of the Coriolis analysis.

In addition to this new FIR data from our lab, several other studies of Ar-H$_2$O have been completed since the development of the AW1 IPS. Lascola and Nesbitt measured infrared combination differences establishing the relative energy of $J = 1$, $\Sigma(10)$ and $J = 1$, $\Pi(10)$, which was not available from direct FIR measurements, to be 11.3333 (3) cm$^{-1}$—only 0.1 cm$^{-1}$ from Cohen and Saykally's prediction on the AW1 surface. Two different internal rotor transitions in para-Ar-D$_2$O and one such transition in Ar-HDO have been studied by Suzuki et al. Zwart et al. have studied an additional two internal rotor transitions in ortho-Ar-D$_2$O. The dipole moments and nuclear quadrupole coupling constants of the complex in the $\Sigma(00)$ and $\Sigma(10)$ states have been measured by Fraser et al.

The Ar-H$_2$O IPS extracted from this new collection of VRT spectra is described at length in a forthcoming paper.

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the anisotropy in the IPS for Ar–H2O is shaped by the same competition between attractive and repulsive anisotropies that governs the structure of the Rg–HX potentials. Both the attractive and repulsive anisotropies are maximized at the orientation Ar–HO, the linear hydrogen-bonded geometry. The anisotropic repulsive forces are sharply localized about the hydrogen atoms which protrude about 0.3 Å beyond the spherical repulsive forces surrounding the oxygen. The anisotropic attractive forces are more slowly varying functions of orientation. Because the attractive forces are not as sharply peaked as the repulsive forces, the potential minimum occurs as near to the hydrogen atom as the repulsive forces allow, viz. \( \theta \sim 90^\circ \). A preliminary version of the new IPS is shown in Figure 7. The three intermolecular coordinates are the vector from the center of mass of the water to the argon (\( R \)), the angle of this vector with respect to the \( C_2 \) axis of \( H_2O \) (\( \phi \)), and an angle describing the rotation of the \( H_2O \) monomer about its \( C_2 \) axis (\( \phi \)). \( \theta = 0 \) is chosen to be the orientation with the argon closest to the hydrogen atoms and on the \( C_2 \) axis. \( \phi = 0 \) is defined as the geometry where all four atoms are coplanar. The IPS has a broad minimum extending from the

linear hydrogen-bonded geometry (\( \theta \) about 55°) to orientations where the \( H_2O \) \( C_2 \) axis is perpendicular to the van der Waals bond axis (\( \theta = 90^\circ \)) and even beyond to \( \theta = 120^\circ \). At values of \( R \) beyond the reach of the exponentially decaying repulsive interaction, the minimum in the surface occurs at the orientation at which the argon approaches along the OH bond. At this orientation the attractive forces are maximized. The usual concept of hydrogen bonding, viz. acidic proton seeking nonbonded electron pairs, is thus followed by the long-range interactions, while repulsive forces induce a reorientation as distances near the van der Waals minimum are approached.

**H2O–CO and H2O–N2.** Bumgarner et al. have studied VRT spectra of the complexes of water with \( N_2 \), and with the isoelectronic species \( CO \). The observed spectra correspond to the \( K_r = 1 \) rotation–tunneling transitions of a near-prolate symmetric top. The energy level diagram for the \( H(D)_2O–CO \) transitions is shown in Figure 8. The results for \( N_2–H_2O \) are similar, although they are complicated by the presence of additional tunneling states associated with the permutation–inversion symmetry of the two equivalent nitrogen nuclei. The anisotropic forces in these systems are much greater than those in the Ar–H2O complex due to the presence of electrostatic interactions (e.g. dipole–quadrupole), of many more anisotropic dispersion terms, and because the cylindrically shaped diatomic molecules have more structure in the repulsive wall than does the spherical argon atom. As a result, the internal motion of the \( H_2O \) molecule is much more strongly hindered. In combination with the microwave spectra obtained by Yaron et al. and by Leung et al., these FIR–VRT spectra have been used to derive structural and dynamical constraints to the motion of the \( H_2O \) and to estimate the equilibrium structure of the complexes. These data have been interpreted with a model that assumes a nearly planar complex and interchange of the hydrogens by a tunneling path localized in the plane. Both clusters are observed to exhibit hydrogen-bonded equilibrium geometries, with the three heavy atoms and one hydrogen arranged in a nearly linear configuration. Interestingly, the equilibrium structure in \( H_2O–CO \) is not completely linear. The evidence presented by Yaron et al. based on their microwave study is further supported by FIR spectroscopy, indicating that the C–HO bond has an equilibrium angle of about 11°. Bumgarner et al. obtain the tunneling frequencies in \( H_2O–CO \) and in \( D_2O–CO \) as 16.7 and 1.0 GHz, respectively, assuming that they are independent of \( K_r \). It is interesting to note that these tunneling

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frequencies are about the same as those associated with donor–acceptor interchange in the water dimer and its fully deuterated isotopomer. These authors interpret the tunneling frequencies to indicate a barrier to the hydrogen interchange motion in H₂O–CO of about 220 cm⁻¹.

CH₄–H₂O and C₂H₆–H₂O: Model Hydrophobic Systems. The interaction of hydrocarbons with water affords an opportunity to investigate important aspects of the hydrophobic effect which are not manifested in the interaction of water with the nonpolar argon atom. For example, the dependence of the IPS on the orientation of the hydrogens of methane and propane should provide specific insights into the nature of the repulsive forces operating between longer chain hydrocarbons and water. FIR–VRT spectra of the CH₄–H₂O and the C₂H₆–H₂O complexes have been obtained by Cohen et al.⁴⁴ and by Steyert et al.⁵⁵ The IPS of methane–water provides an interesting opportunity to investigate the importance of high-order electrostatic contributions (e.g. dipole–octupole and dipole–quadrupole interactions) to the IPS. These electrostatic forces are not present in the interaction of argon with water and are so weak that they are typically neglected in studies of more strongly bound systems, such as the water dimer or the HF dimer. They are, of course, the lowest nonzero contribution to the attractive forces in H₂O–CH₄.

Cohen et al.⁴⁴ have observed and assigned six different VRT bands of CH₄–H₂O in the region from 18 to 18.5 cm⁻¹. A stick spectrum of the rotationally assigned lines which belong to CH₄–H₂O. Perturbations either in the energy level patterns or in the intensities prevent assignment of these other bands at this time. The high-resolution spectra of the rotationally assigned lines is shown in Figure 9. Perturbations in a complex manner. In some cases, the tunnelings interfere destructively to give a small splitting. Assignment of a-type rotation–tunneling transitions at 22 cm⁻¹ by Busarow et al.⁴⁷ provided the first direct experimental information on these transitions. These tunneling modes affect the energy level patterns of states with different symmetries in a complex manner. In some cases, the tunnelings interfere constructively to give a large splitting, while in others they intere destructively to give a small splitting.

FIR spectra were critical to determining the A rotational constant and the size of the largest tunneling interaction constant (denoted hₘ) in the water dimer. Measurement of perpendicular Kₐ = 2 rotation–tunneling transitions at 22 cm⁻¹ by Busarow et al.⁴⁷ provided the first direct experimental information on these transitions. These measurements are indicated in Figure 10. They occur among levels of A₂ and B₂ symmetry in Kₐ = 1 and Kₐ = 2. The R(4) B₂⁺ line of these transitions is shown in Figure 9. Subsequent measurement of Kₐ = 1–0 transitions by Fraser et al.⁴⁷ and by Steyert and Shaik⁴⁸ and their co-workers allowed the separation of the effects of the rotation about the A axis of inertia from the extremely facile hₘ tunneling motion. Zwart et al.⁴⁹
have also measured some transitions in the $K_v = 2 \rightarrow 1$ band which were not found in the work of Busarow et al. In the fit of Coudert and Hougen, the $A$ rotational constant is determined to be 196 GHz and $h_{\alpha}$ is determined to be $-50$ GHz. The spectroscopic results have been reviewed by Fraser.

The complexity of the multidimensional intramolecular dynamics has thus far precluded any direct understanding of the relationship of the VRT spectra to the IPS for (H$_2$O)$_2$. However, assuming that all tunneling barriers are large compared to the tunneling splittings, Coudert and Hougen have developed a model that provides some insight into the intermolecular dynamics. They have fit all of the available VRT data to a model that includes several different types of tunneling splittings. It should be noted that the large $h_{\alpha}$ splitting suggests that the high barrier approximations of ref 105 may not be sufficiently accurate to describe the intermolecular dynamics in the vibrational ground state. In excited VRT states it is virtually assured that this approximation will be inadequate, thus requiring development of new dynamical methods.

The four different tunneling motions implicated in the analysis of Coudert and Hougen are (1) the interchange of hydrogens on the proton acceptor, (2) geared interconversion of the roles of donor and acceptor, (3) antigeared interconversion of the donor acceptor roles, and (4) interchange of the hydrogens on the hydrogen bond donor and on the hydrogen bond acceptor without interconversion. Tunneling splittings associated with the interchange on the proton acceptor contribute on the order of 6 cm$^{-1}$ (180 GHz) to the observed splittings; the tunneling splittings contribute less than 1 cm$^{-1}$: approximately 0.66, 0.05, and 0.05 cm$^{-1}$, respectively. The initial theoretical models of Coudert and Hougen assumed that only the first two of these motions were relevant, based on analogy to (HF)$_2$ and using the model water dimer IPS of Reimers, Watts, and Klein (RWK2) as a guide to understanding likely dynamical pathways and barriers to rearrangement of the hydrogens within the molecule. The permutation associated with the $h_{\alpha}$ tunneling constant is thought to be the interchange of the two hydrogens on the hydrogen bond acceptor. Coudert and Hougen have suggested that this tunneling occurs, not by internal rotation of the acceptor about its $C_2$ axis, but by a more complex path involving downward motion of the hydrogen bond acceptor, through a configuration in which it is coplanar with the hydrogen bond, and the simultaneous internal rotation of the hydrogen bond donor.

A similar pathway has been invoked to describe tunneling in methylamine. The barrier to the simpler internal rotation of water about its $C_2$ axis is on the order of 1000 cm$^{-1}$ on the RWK2 IPS. This is too high to be consistent with the size of the observed tunneling splitting. On this same potential, the methylamine-type motion is hindered by a barrier of about 130 cm$^{-1}$.

Smith et al. have presented ab initio calculations of the barriers on the water dimer IPS. These authors find the barrier to methylamine-type motion to be 200 cm$^{-1}$ and the lower barrier to donor-acceptor interchange to be 300 cm$^{-1}$. This second barrier is much lower than the 800-cm$^{-1}$ barrier to donor-acceptor interchange identified by Coudert and Hougen on the RWK2 surface. Even if we assume that the ab initio calculations could underestimate the barriers by 100%, the disagreement between a high-quality empirical surface and high-quality ab initio theory is still very large. The empirical potential substantially overestimates the barrier at this geometry. Clearly, much work remains to be done in order to clarify the nature of the permutation tunneling in the water dimer.

Isotopomers of (H$_2$O)$_2$ have also been studied in the microwave region, providing various dynamical constraints on the IPS through varying one or more of the masses and measuring the effect on the tunneling splittings. In (D$_2$O)$_2$, the tunneling splittings are reduced by an order of magnitude from those of the fully protonated isotopomer, viz. from 15–20 to 0.9–1.1 GHz. In the FIR region, Zwart et al. have measured two $K_v = 2 \rightarrow 1$ bands in (D$_2$O)$_2$. As in (H$_2$O)$_2$, these bands allow determination of the $A$ rotational constant and the $h_{\alpha}$ tunneling splitting. In the ground state of (D$_2$O)$_2$, all the splittings are sufficiently small to justify the use of the high barrier limit model of Coudert and Hougen.

Intermolecular vibrations of the water dimer are predicted to lie above 100 cm$^{-1}$—a region of the spectrum which has not yet been explored using laser-based methods because of inadequate sensitivity. Taking advantage of state of the art detector technology, Puglino et al. have measured a $c$-type torsional vibration in (D$_2$O)$_2$ at 85 cm$^{-1}$, possibly corresponding to the lowest vibration in the methylamine-like tunneling coordinate. The donor-acceptor interchange tunneling splittings are increased in this level by about a factor of 12, and there is a significant contribution from interconversion tunneling without interchange. This suggests that the tunneling coordinates are strongly coupled to the vibrational coordinate and that the VRT spectra thus provide a significant dynamical constraint to the IPS in several coordinates. In any case, this work constitutes the first detailed study of an

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intermolecular vibration in the important water dimer system. Hopefully, more will soon follow.

NH3-containing Clusters

Many ammonia-containing dimers have been studied by Klemperer and co-workers in the microwave region. Contrary to the initial expectations and to intuition developed from the study of the liquid-phase behavior of ammonia and amines, ammonia does not act as a hydrogen bond donor in any known gas-phase dimer. Even in (NH3)2, Nelson et al. have shown that there is no apparent tendency for either monomer to point a hydrogen at the lone pair of its partner. This is an extraordinary result which demands that we rethink the basic concept of hydrogen bonding. Experimental IPS's for dimers containing NH3 are a natural starting point for attempts to understand and explain the apparent differences in behavior between liquid-phase ammonia and ammonia as a binding partner in gas-phase dimers.

Ar-NH3: Effects of Inversion Motions on Intermolecular Potentials

The microwave spectrum of Ar-NH3 was first investigated by Fraser et al. and by Nelson et al. who reported the observation of a large number of transitions for this cluster in the vicinity of the free NH3 inversion frequency. This is the only NH3-containing cluster for which evidence of umbrella inversion within the cluster has been presented. In all other systems, the inversion tunneling is apparently quenched. Nelson et al. were able to assign pure rotational transitions of Ar-NH3 in the ground-state radial wave function. The first averaged over the ground-state radial wave function. The first an effective angular potential

the data place limits on the range of effective potentials for the coordinate, reflecting substantial penetration of the hydrogens beyond the spherical electron distribution of the monomer. Experimental surfaces which do not explicitly include terms which represent this repulsion, such as those presented by Schmuttenmaer et al., may only fortuitously reproduce the data. On the other hand, the ab initio surfaces are not capable of reproducing the experimentally determined VRT energies or expectation values. This may be due to an overestimation of the contribution of anisotropic repulsive forces near the minimum, an underestimate

References


Figure 12. Ar-NH3 energy levels and the observed transitions (ref 65).
of the contribution of anisotropic dispersion forces, or perhaps both. van Bladel et al.\textsuperscript{121} have attempted to modify the ab initio potential of Bulski et al.\textsuperscript{120} to improve agreement with experiment by adopting a single scaling parameter for the anisotropic repulsion. This adjusted surface is in much better qualitative agreement with experiment, suggesting that the ab initio surface does provide a useful starting point for the development of an IPS which accurately models the experimental data. Schmuttenmaer et al.\textsuperscript{122} have since measured additional VRT transitions from which a quantitative 3-dimensional surface is currently being extracted\textsuperscript{122} with the use of the collocation method.

\textbf{NH}_3^-\textbf{NH}_3^-: A Hydrogen-Bonding Anomaly. The rotational spectrum of the ammonia dimer was first observed by Nelson et al.\textsuperscript{116,117} Nelson and Klemperer\textsuperscript{118} then used permutation-inversion group theory to establish that 10 different symmetry tunneling sublevels exist in this complex. However, only two sets of pure rotational transitions would be expected to occur among states of G symmetry. All other transitions within the ground vibrational level obey rotation–tunneling selection rules and thus occur at higher frequencies. The pure rotational transitions observed by Nelson et al. were assigned to 4-fold degenerate VRT states.\textsuperscript{116,117} The interpretation of the results of Nelson et al. has been particularly controversial, as they establish a structure for the dimer which does not exhibit a hydrogen bond. Nuclear quadrupole hyperfine coupling constants in several different isotopomers have been used to show that the two subunits are on the average inequivalent, with their \( C_3 \) axes oriented at angles of 49° and 115° with respect to the van der Waals bond axis (\( R \)).

Although the isotope data obtained by Nelson et al. make it seem quite unlikely that vibrational averaging is responsible for the observation of a non-hydrogen-bonded structure in this molecule, Liu et al.\textsuperscript{123} and others\textsuperscript{122,124} initially challenged the interpretation of the microwave spectra by Nelson et al., suggesting that such averaging does indeed cause the apparent structure to deviate significantly from the equilibrium value. More recent ab initio calculations\textsuperscript{125} have found the structure proposed by Nelson et al. to be a global minimum. This structure has been rationalized by some as being a doubly hydrogen bonded structure.

The complex nature of the hydrogen permutation tunneling in (NH\(_3\))\(_2\) has not yet been characterized. Two types of permutations are thought to be involved: (1) the interchange of the roles of the two inequivalent NH\(_3\) subunits and (2) exchange of the positions of hydrogens on the individual NH\(_3\) monomers by C\(_3\) rotation about the monomer symmetry axis (or its equivalent). These permutations may occur in the complex via one or more dynamical pathways. No reliable estimates of the splittings associated with these motions are available from either theory or experiment. Nelson et al. suggested the tunneling splittings occurred at frequencies above 30 GHz, since no unassigned transitions attributed to (NH\(_3\))\(_2\) were observed in either MBER or FTWM experiments.

Havenith et al.\textsuperscript{126} have measured transitions to the lowest excited intermolecular vibrational level of NH\(_3\) dimer, near 20 cm\(^{-1}\). Six different VRT subbands were measured, which sample all of the different symmetries which are predicted by group theory. The symmetry assignments of some of these transitions have since been reassigned by Loeser et al.\textsuperscript{127} The energy level differences obtained in this work are shown in Figure 13 with the corrected symmetry labels. Two of the transitions have been identified as originating in the \( G \) ground states observed by Nelson et al. and one in a \( K = 1 \) G state while the others are assigned to states of A and E symmetry. These spectra raise some interesting questions regarding the unusual dynamical behavior of this molecule. For example, if the first excited vibrational level of the complex occurs at 20 cm\(^{-1}\), then how large is the tunneling splitting in this same coordinate? The spectra of Havenith et al. only begin to characterize the many different VRT splittings in the ground and the first excited states of the complex. They do not sample enough common states to determine any of the tunneling splittings. Additional data obtained by Loeser et al.\textsuperscript{128} and by Zwart\textsuperscript{129} contain enough common levels to establish the relative energies of several \( K \) = 0 and 1 levels. At the time of this writing, seven different \( K \) = 1 \( \leftrightarrow \) 1 transitions have been observed out of the eight which are expected. The measured separation between the lowest \( K \) = 1 and \( K \) = 0 levels ranges from 190 to 290 GHz and is clearly much larger than the value (130 GHz) estimated from the structural A rotational constant. This implies a significant contribution to the \( K \) = 1 energies from VRT dynamics. Loeser et al. have also presented a complete mapping of the \( K = 0 \) and \( K = 1 \) and some of the \( K = 2 \), \( v = 0 \) and \( v = 1 \) G state levels. These G state spectra demonstrate the complete breakdown of assumptions based on a high barrier tunneling limit, such as that used successfully by Coudert and Hougen to describe (H\(_2\)O)\(_3\) intermolecular dynamics. Transitions which are forbidden in the high barrier limit are observed to be quite strong. Unfortunately, the absence of a suitable dynamical model has thus far precluded a detailed understanding of (NH\(_3\))\(_2\) and its spectra, although the wealth of data provided by Loeser et al. should stimulate new efforts in this direction.

\textbf{HX-Containing Clusters (X = F, Cl, Br, CN)}

\textbf{Rare Gas–Hydrogen Halides.} The measurement of the FIR– VRT spectrum of Ar–HCl\textsuperscript{25,30,31,32} and the subsequent determination of the H\(_6\)(3) IPS from this data by Hutson\textsuperscript{33} were discussed above. Since the development of the H\(_6\)(3) IPS, the Ar–HCl spectrum has been more extensively studied. Busarow et al.\textsuperscript{32} measured the \( \Sigma (j=1) \) vibration in a CW planar jet using the TFIR laser. The II(\( j=1 \)) band has been reinvestigated by Leopold et al.\textsuperscript{35} in a CW planar jet, and McKellar et al.\textsuperscript{36} have measured FT–FIR spectra of Ar–HCl formed at equilibrium in a cooled multipass cell. Hutson\textsuperscript{33} has predicted that a second set of bending transitions correlating to the \( j = 2 \) internal rotor level should be observable. These states would provide the most new information about the IPS, but to our knowledge they have not yet been searched for in the FIR region.

In the FIR region, the only other rare gas–HX system studied in detail is Ar–HBr. Firth et al.\textsuperscript{37} observed the II(\( j=1 \)) transition nearly exactly at the frequency predicted by Hutson\textsuperscript{33} using an IPS extracted solely from microwave rotational data. Hot bands assigned to the intermolecular stretching vibrations of Ar–HF and Kr–HF have been measured in the near-infrared spectra by Fraser
and Pine.\textsuperscript{55} By utilizing these spectra along with the measurement of the van der Waals stretch-HF chemical bond stretch combination band observed by Lovejoy and Nesbitt,\textsuperscript{180} the ground-state stretching frequency of Ar-HF is established to be 38.6863 cm\textsuperscript{-1}. Very recently, the Ar-HF complex has also been observed in the FIR region by Leopold and co-workers.\textsuperscript{58}

The most extensive studies of a series of the rare gas-HX clusters are the near-infrared measurements of Nesbitt and co-workers, who have measured VRT spectra built on the HF (DF), and HCl (DCI)\textsuperscript{128-133} chemical bond stretches of these species clustered with He, Ne, and Ar. The spectra are rich in information about the anisotropy in the intermolecular potential and the coupling of the bound van der Waals VRT levels on the $\nu = 1$ IPS to the dissociative continuum on the $v = 0$ IPS. Experimental potentials have been derived only for Ar-HF ($v = 1$) and for Ar-HCl ($v = 1$),\textsuperscript{129} although others are no doubt forthcoming. The Ar-HF surface was determined using the rotational RKR method of Child and Nesbitt,\textsuperscript{133} which relies on the approximate separability of the angular and radial degrees of freedom. This approximation may hold for Ar-HF but has been shown to fail markedly in several other similar complexes in which the repulsive sphere surrounding the hydrogen atom penetrates beyond that of the heavy atom (viz. Ar-HCl,\textsuperscript{31} Ar-H$_2$O,\textsuperscript{37,38,61} Ar-NH$_3$,\textsuperscript{43})

The Ar-HCl ($v = 1$) surface has been extracted by Hutson\textsuperscript{134} from the experimental data of Lovejoy and Nesbitt\textsuperscript{131,132} in a fit similar to the one performed for Ar-HCl ($v = 0$),\textsuperscript{51} and the resulting surfaces are nearly identical. The complex is bound 1.6 cm\textsuperscript{-1} more strongly in the vibrationally excited state at an equilibrium bond distance 0.01 Å longer than in the ground state. An ab initio surface has been computed for Ne-HF, and the VRT spectrum has been calculated on this surface.\textsuperscript{136} The qualitative agreement of prediction on the ab initio IPS with experiment indicates that it has an anisotropic component which approximately reflects the essential physics in the cluster. However, the binding energy on the ab initio IPS has been shown to be roughly 30% too shallow, and a rigorous experimental determination of the IPS which would permit a detailed analysis of the accuracy of the ab initio IPS has not yet been presented.

Ar-HCN. Fraser and Pine\textsuperscript{37} have measured the fundamental intermolecular bending vibration of Ar-HCN in the near-infrared region in combination with the CH stretching vibration. The bend was observed to be 7.79 cm\textsuperscript{-1} above the CH stretching band of the cluster. This same intermolecular vibration has recently been observed at 6.07 cm\textsuperscript{-1} by Cooksy et al.\textsuperscript{128} built on the ground vibrational state of the monomer.\textsuperscript{61} These observations are in rough agreement with the prediction made by Leopold et al.\textsuperscript{138} who estimated the bending frequency to be 10 cm\textsuperscript{-1} based on analysis of the unusual isotope shifts and large size of the centrifugal distortion in the ground state. Leopold et al. have also suggested that the Ar-HCN complex exhibits strong angular-radial coupling, since the argon can approach much closer to the center of mass from the side of the molecule than from an end-on direction. Calculations by Madenovic and Bacic\textsuperscript{139} on an ab initio surface provided by Dyksstra\textsuperscript{140} also evidence the strong effects of angular-radial coupling. However, these authors compute the bending vibration to lie 12.5 cm\textsuperscript{-1} above the ground state, indicating that the ab initio surface is too steep in the bending coordinate. Calculations by Clary et al.\textsuperscript{141} predicting the first $\pi$ bend to be at about 6.6 cm\textsuperscript{-1} are in better agreement with experiment.

Ar$_2$-HCl: A Direct Probe of Three-Body Forces. Three-body forces clearly make important contributions to the properties of solids and liquids. However, there is virtually no experimental information which provide accurate constraints on the sizes, shapes, or sources of these forces. Recent efforts by Chalisinski et al.\textsuperscript{142} to calculate three-body forces by ab initio techniques are consistent with the notion that there are many contributions to them which fortuitously cancel to give a net effect which is small. These calculations show explicitly that the success of the Axilrod-Teller expression\textsuperscript{2} in reproducing the effective form of three-body intermolecular forces is due to such a fortuitous cancellation of many

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
\textbf{Frequency (cm$^{-1}$)} & \textbf{Assignment} \\
\hline
35 & \text{AR$_2$-HCl} \\
37 & \text{AR$_2$-HCl} \\
39 & \text{AR$_2$-HCl} \\
\hline
\end{tabular}
\caption{Observed frequencies of the AR$_2$-HCl complex.}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{(a, top) Calculated stick spectrum of the mixed bend/stretch band of AR$_2$-HCl and (b, bottom) the $3_1 \leftrightarrow 2_0$ line from that band (ref 73).}
\end{figure}

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\textsuperscript{133} Lovejoy, C. M.; Nesbitt, D. J. Chem. Phys. 1990, 93, 5387.
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different types of three-body interactions.

Intermolecular VRT spectra have been assigned for only two trimers, Ar₂-HCl and (HF)_2, which is discussed below. Ar₂-HCl is of particular interest since the pair potentials for argon dimers and Ar-HCl are both accurately known. Extraction of the three-body forces operating in this cluster can proceed by determining the difference between the experimental 5-dimensional IPS and the sum of the pairwise forces. Elrod et al. have observed two of the low-lying VRT states of Ar₂-HCl at 37.2 and 39.5 cm⁻¹ above the ground state. These measurements constitute a powerful demonstration of the sensitivity of the TFFIR laser/CW Planar jet apparatus. Over 400 VRT lines have been assigned, many with resolution of quadrupole hyperfine structure, as shown in Figure 14.

Ar₂-HCl was first identified by Klots et al. using a Fourier transform microwave spectrometer. In its ground state, this cluster is T-shaped, with the hydrogen of HCl pointing toward the center of the line connecting the argons. Ar₂-HCl has five intermolecular degrees of freedom (R, ρ, χ, θ, φ). As in other rare-gas complexes with hydrides, the anisotropy in the IPS is expected to break the (2j + 1) spatial degeneracy of each free rotational level of the monomer, but not to extensively mix them with other internal rotor levels. Six low-lying intermolecular vibrations are expected: the Ar–Ar stretch (ρ), the (Ar₂)–HCl stretch (R), the (Ar₂) bend (χ), and three bending levels (θ, φ), associated with the j = 1 internal rotor level of the HCl monomer. The three HCl bending levels have been denoted the parallel bend, in-plane bend, and the out-of-plane bend by Hutson et al. The parallel bend correlates to the m_j = 0 component of the j = 1 internal rotor state, and the other two bends are linear combinations of m_j = ±1 and m_j = −1.

The calculations of Hutson et al. demonstrate that the VRT spectrum of the complex depends strongly on the nature of the three-body forces which contribute to the IPS. However, the dynamical approximations employed by Hutson et al. have been shown by the experimental study of Elrod et al. to be too severe, as was suggested by Hutson et al. themselves.

The measured VRT spectra are assigned to the parallel bend and to a state which is an admixture of in-plane bending, one or more of the stretching motions, and perhaps the (Ar₂) bend. This second VRT band evidences strong coupling among the different intermolecular coordinates. It strongly suggests that a fully coupled 5-dimensional solution to the Schrödinger equation is necessary to accurately compute the spectra on a trial IPS. Analysis of 35Cl and 37Cl spectra allows a determination of whether the HCl points toward or away from the argon pair in the excited states. In the excited parallel bending state, the hydrogen points away from the argons. This is analogous to the result obtained for Ar₂-HCl, where the ground state samples the primary minimum of the ab initio potential surface with the axis of the HC₁ bond tilted 60° from the hydrogen bond. In the ground vibrational state, the tunneling associated with exchanging the donor–acceptor roles causes a 0.7 cm⁻¹ splitting. VRT spectra of the HF dimer have been collected by Quack et al. using a FTIR spectrometer in the range 100–550 cm⁻¹. A complex spectrum was observed, only parts of which have been assigned thus far. The assignments include two transitions terminating in the K = 3 level of the geared interchange vibration (also called the disrotatory in-plane vibration and the trans bending vibration) at 275.4 and 157.1 cm⁻¹ and two subbands terminating in the out-of-plane torsional mode at 399.78 and 400.75 cm⁻¹. The geared interchange vibration corresponds to excitation in the same coordinate as that which describes the permutation tunneling. Dayton et al. have provided a precise determination of the binding energy of the cluster, D_b = 1062 ± 5 cm⁻¹. This is a useful constraint for determination of an experimental IPS, since most VRT spectra are only weakly sensitive to the absolute well depth.

There has also been a considerable theoretical effort aimed at developing an IPS for the HF dimer and at understanding the dependence of the IPS on the intramolecular coordinates. Much of this work has been reviewed recently by Truhlar. Theoretical studies of this tunneling motion by Bunker et al., using an ab initio potential surface, have provided a qualitative explanation for the variation of the tunneling splitting as a function of K_v. These calculations indicate that the ab initio surface represents much of the physics of the interaction correctly. However, the agreement is far from quantitative. An empirical IPS has been presented by Barton and Howard, based on a fit to some of the early microwave results. Much more data have been acquired since the development of this surface, and it is an opportune time to consider developing an empirical IPS from the available VRT data. We note, in this respect, the recent efforts of Marshall et al., who have calculated accurate eigenvalues on an ab initio surface, using close-coupling methods. This 4-dimensional calculation is too expensive to be embedded in a least-squares routine at this time, but it will serve as a benchmark for testing the accuracy of more efficient methods. In another effort, Quack and Suhm have calculated a few VRT eigenvalues on a model surface using quantum Monte Carlo techniques.

(HCl)_2 (HCl), has a structure similar to that of the HF dimer, except that the nonbonded hydrogen is oriented at an angle of 90° to the hydrogen bond. The HCl dimer is also much more weakly bound; the binding energy has been measured by Howard and Pine to be 430 ± 22 cm⁻¹. As a result, interchange tunneling in this molecule is vastly more facile than in the HF dimer. Blake and Bumgarner have directly measured the splitting associated with this motion to be 15.48 cm⁻¹—more than 10 times the 0.7 cm⁻¹ splitting in (HF)_2. The rotation–tunneling spectrum of the HCl dimer in its ground state has been studied by Blake et al., who measured K_v = 1−K_v = 0 rotation–tunneling spectra at 26 cm⁻¹, and by Moazzen-Ahmadi and co-workers who reported higher K_v transitions. Analysis of the complex hyperfine structure, such as that shown in Figure 15, by Blake et al. established that the A rotational constant is about 7.5 cm⁻¹ and that the complex is planar to within 10°. The only van der Waals vibration thus far studied in this cluster is the out-of-plane torsional mode, observed by Moazzen-Ahmadi et al. near 165 cm⁻¹ with FIR methods. An extensive ab initio effort to understand the structure and dynamics of HCl dimer has also been mounted. This work has included calculation of the interaction energy at many points.
on the surface and computation of the $K_v$ dependence of the tunneling splittings on that surface. The ab initio calculations are less successful at predicting the tunneling dynamics than in the HF dimer because of the more significant coupling among the different intermolecular degrees of freedom and the low ($\sim 70$ cm$^{-1}$) barrier to tunneling.

(\text{HCN})_2 and HCN--HF. HCN dimer and HCN--HF are also simple models for hydrogen bonding. Both molecules adopt a linear structure as expected for hydrogen-bonded dimers. They have three intermolecular vibrations—two doubly degenerate bends and a stretching vibration. Jucks and Miller\textsuperscript{70} have measured the van der Waals stretching fundamental in the HCN dimer by infrared combination differences to be $40.751$ cm$^{-1}$. In the CH stretching excited state the van der Waals stretching frequency is $40.552$ cm$^{-1}$. Hot bands assigned as originating in the two different bending vibrations of this complex have been observed, but these have not been tied to the ground state by measurement of combination bands, and the VRT frequencies remain unknown. All of the fundamental vibrations of the related complex, HCN--HF, have been obtained by a combination of laser and Fourier transform spectroscopies through the work of Bevan and co-workers\textsuperscript{71} as well as others. The three intermolecular modes are assigned as the intermolecular stretch, $168.2$ cm$^{-1}$, and two intermolecular bends at $550.03$ and $78.58$ cm$^{-1}$.

(HF)$_3$. The HF trimer is a cyclic hydrogen-bonded cluster. In elegant double-resonance experiments, Kolenbrander et al.$\textsuperscript{72}$ have measured two torsional VRT bands of the HF trimer. These are the overtone of the in-plane torsion at $940.5$ (2) cm$^{-1}$ and the in-plane, out-of-plane torsional combination band at $954.5$ (2) cm$^{-1}$. These experiments were interpreted by comparison with an ab initio treatment of the intermolecular forces and an approximate treatment of the VRT dynamics using the ab initio force field. The model calculations predict infrared-active torsional fundamentals at $491$ and $508$ cm$^{-1}$.

Clusters of Reactive Species

Free radicals and molecular ions are the species which determine the course of most chemical reactions. However, because of their extreme reactivity, relatively little is known about these species. Even less is known about the intermolecular forces which govern their behavior in condensed phases. Few experiments have been capable of providing information about intermolecular forces in clusters of reactive species. In recent work, Lee and co-workers\textsuperscript{154--158} have studied the high-frequency intramolecular vibrations of isolated mass-selected clusters, including species of the forms $\text{H}^+\text{(CH}_2\text{O)}_m\text{H}^+\text{(NH}_3)_m\text{H}^+(\text{H}_2\text{O})_m\text{(NH}_3)_m$ and $\text{H}^+(\text{H}_2\text{O})_m$. The spectra for the smallest of these systems were obtained with partial rotational resolution, allowing some structural information to be obtained. By far the most extensive experimental studies of clusters containing a reactive molecule are those of Ar--OH\textsuperscript{73,159--165}. Less detailed spectra of Ne--OH\textsuperscript{164}, Kr--OH,\textsuperscript{166} and Ne--CN\textsuperscript{168} have also been reported. Radical-containing clusters such as these exhibit unusual quantum numbers and angular momentum coupling. Dubernet et al.$\textsuperscript{169}$ have described the angular momentum coupling in clusters of an atom with a linear radical, showing how

\begin{itemize}
  \item[(167)] Heaven, M. C. Private communication.
\end{itemize}
to develop a qualitative description for the energetics and intensities of VRT transitions in these complexes and how to relate the VRT spectra to the anisotropic intermolecular forces.

Initial investigations of Rg-OH spectra were obtained by laser-induced fluorescence, in the groups of Lester,159-163 and Heaven.164,165 VRT spectra in the first excited electronic state (A^2E) of Ar-OH and Ar-OD were measured in that work. The most pronounced features in the spectrum correspond to an extended progression in the intermolecular stretching vibration on the excited electronic surface. Intermolecular bending vibrations built on the electronic transition were also observed. The extended stretching progression results from the large geometry change upon electronic excitation. The equilibrium bond length in the ground state is about 3.6 Å; in the excited state it is nearly 1 Å shorter! The excited-state surface is also much deeper. Ab initio calculations by Degli-Esposti and Werner suggest a ground-state binding energy of 70 cm\(^{-1}\) and an excited-state binding energy of 1095 cm\(^{-1}\). The VRT spectra in the A^2E excited state have been analyzed by Bowman et al.171 They obtain an experimental IPS exhibiting an absolute well depth of 1061 cm\(^{-1}\), in reasonable agreement with the ab initio value. The observed data sample primarily the Ar-HO geometry, and as a result, the potential is not accurately determined at the Ar-OH geometry. These experimental spectra have subsequently been extended by Beck et al.162 to include overtone spectroscopy of Ar-OH(v=2). Recent experiments by Chang et al.165 and Schliepen et al.166 have measured the electronic spectra at much higher resolution, probing both the A-doubling and of the hyperfine interactions within the cluster. These properties are a sensitive probe of the VRT wave function and will allow a much more accurate characterization of the excited-state IPS than was otherwise possible.

In the most recent experiments, Berry et al.17 have observed spectra of several different ground-state (X^2II) VRT levels, including the first four bending levels, the fundamental (n = 1), and the overtone (n = 2) of the intermolecular stretch and several bend-stretch combination levels, by stimulated emission pumping (SEP) techniques. These experiments sample an extended region of the ground-state surface and should permit a direct fit for the purpose of extracting an empirical IPS from the experimental data. Bound bending and stretching levels are observed well above the ab initio dissociation limit, establishing that the ab initio surface of Degli-Esposti and Werner170 severely underestimates the binding energy (at least 30%). The experiments of Berry et al. also show that while the ab initio surface is useful for predicting the gross features of the spectrum, it only qualitatively represents the anisotropy in the IPS. For example, predictions of the first four intermolecular bending eigenvalues by Berry and Clary172 on the ab initio IPS do predict the correct energy level ordering and approximate spacing, but they differ by as much as 20% from the experimentally measured energy differences.

Hydrogen-Containing Clusters

Because of their weak binding energies and the large rotational constants of both the monomer and the complex, clusters containing H\(_2\) are spectroscopically unique. H\(_2\) clusters are especially important in astrophysical modeling of dense clouds and planetary atmospheres. The spectra and IPS's of these clusters have been discussed by McKellar,173 Hutson,174 Nesbitt,175 and Hutson and LeRoy,176 among others. McKellar has obtained new spectra of Rg-\(^{1}H_2\) complexes175 corresponding to j = 2 ↔ j = 0 and j = 3 ↔ j = 1 internal rotor transitions of H\(_2\) within the complex. These spectra provide precise constraints with which to improve upon, the already highly accurate Rg-H\(_2\) surfaces of LeRoy and Hutson.174 Calculations of pressure broadening cross sections on these surfaces by Green175 also indicate regions of the surface which can be improved. McKellar173 has also obtained extensive spectra of the H\(_2\) dimer and various isotopomers. These VRT spectra may be compared with the calculations of Danby,176 on the ab initio M8O (H\(_2\)) IPS which has been obtained by Meyer et al.177 Significant discrepancies exist. The extensive data set and modern computational methods should permit extraction of the IPS for this complex from the available experimental data.

Other Systems

An Ar-CO\(_2\) intermolecular bending vibration, 27.82 cm\(^{-1}\) above the CO\(_2\) monomer or bending vibration upon which it is built, was observed by Sharpe et al.178 Calculations by Peet179 of the Ar-CO\(_2\) VRT spectrum on a potential surface developed by Hough and Howard179 for CO\(_2\) (000) interacting with argon predict the first bending state to be 31.5 cm\(^{-1}\) above the ground state. Dai et al. have measured extensive VRT spectra of Ar-glyoxal and Ar-glyoxal using elegant SEP techniques.180 Efforts in that group are currently under way to extract the full 3-dimensional IPS of Ar-glyoxal from the VRT data.

Conclusions

In his 1988 review, Nesbitt181 showed that the number of clusters which had been studied by high-resolution spectroscopy has been rising exponentially for over 10 years. Most of these data sample only in the region of the potential minimum. As a result, the interpretation of these spectra in terms of fundamental intermolecular and or molecular properties has not paralleled the explosive increase in the available data. The experiments reviewed in the preceding pages represent an exciting new opportunity in the study of intermolecular forces because they do probe a wide region of the IPS with precision and specificity. It is evident from the preceding discussion that VRT spectra which sample a sufficient region of the IPS to allow experimental determination of the surface can now be obtained quite routinely using a variety of methods. Additional studies employing these methods will no doubt be forthcoming. Accurate experimental intermolecular potentials have now been determined from VRT data for several prototype systems, including Ar-HCI(v=0 and 1),134 Ar-HF(v=1),134 Ar-H\(_2\)O19,29 These anisotropic potentials are expected to be accurate over the full range of intermolecular coordinates sampled by the experimental data. In addition, the anisotropic potentials for Ar-HCI and Ar-H\(_2\)O have been constrained to reproduce long-range attractive forces which are known from other experiments. These potentials are expected to be accurate at intermolecular separations larger than those sampled by the experimental data. IPS's for more complex systems, such as the hydrogen halide dimers, Ar\(_2\)-HCl, and the dimers of hydrogen, water, and ammonia will no doubt be generated soon.

In order for this to occur, computational methods capable of solving for the eigenvalues of the non-linear motion in systems with more than three internal degrees of freedom with both high accuracy and high efficiency must be developed. Both the collocation method90-93,96 and the discrete variable representation (DVR)11,12,13,182-184 have recently been proposed as possible methods for obtaining the eigenvalues of systems with many coupled degrees of freedom. These methods have proven to be highly successful in the calculation of the eigenvalues associated with dynamics in two van der Waals degrees of freedom, viz. Ar-HCI,184 Ar-HCN,134 and Ar-CO\(_2\). The DVR has been

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used in the calculation of dynamics in three dimensions for chemically bound systems. The collocation method has the considerable advantage that it can incorporate nondirect product basis functions such as the spherical harmonics. This aspect of the method is exploited in our recent analysis of the Ar-H2O cluster which exhibits van der Waals dynamics in three dimensions (Ref 90 and 91). These computational methods, and perhaps others, may permit extraction of many-dimensional IPS's from experimental data when further algorithmic improvements are made or faster supercomputers become available. Detailed as-


ARTICLES

Spectroscopic and ab Initio Study of the Interaction of Molecular Hydrogen with the Isolated Silica Hydroxyls and Related Systems

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Experimental vibrational data concerning the interaction of dihydrogen with the isolated hydroxyl of amorphous silica are compared with the results of ab initio calculations, both Hartree–Fock and correlated through perturbative technique (MP2). Silanol (H3SiOH) is chosen to mimic the silica free hydroxyl. Two modes of interaction are considered, one envisaging dihydrogen as a proton donor to the oxygen atom in SiOH (structure F), the other as a proton acceptor in a T-shaped structure (structure T). Calculated properties are the binding energy, frequencies of vibrational motions in the harmonic approximation, and H–H infrared intensity in the double-harmonic approximation. Both structures are stable. Structure T is more weakly bound and has less IR active H–H stretch than structure F, whose calculated features are in better agreement with the experiment. Experimental results concerning the bridging hydroxyl of H-mordenite are also reported. Structures F and T are compared with the known gas-phase complexes of molecular hydrogen.

Introduction

In recent years, Kazansky and co-workers have shown that dihydrogen can be efficiently employed in low-temperature IR surface studies to reveal pairs of acid–base Lewis sites in aluminas and zeolites. The perturbation suffered by the H2 molecule breaks the local symmetry, so rendering its stretching mode IR active (the more so the stronger the interaction), and causes a red shift of the frequency, which is also a measure of the strength of the interaction. In the presence of very strong acid–base pairs dihydrogen may break up heterolytically.

Dihydrogen also interacts with surface hydroxyls. Detailed studies of the interaction of H2 with the free hydroxyl of amorphous silica and zeolites, inclusive of the H–H modes, have shown that at low coverages a definite adduct is formed. Two other cases are known where the interaction of molecular hydrogen and silica is instead nonspecific: (i) the perturbation of hydroxyls in Vycor glass brought about by hydrogen physisorption, very recently studied in the near IR, which takes place at higher coverages than in the previous case; (ii) the trapping of molecular hydrogen by SiO2-based fibers, which interferes with their optical performances. As silica notoriously exhibits acidic properties only, the interaction mechanism is probably different from that observed in the case of acid–base pairs and is basically still to be understood: this is the theme of the present paper. To this purpose, we report and discuss both spectroscopic measurements and computational results. The systems investigated on the experimental side are again the isolated hydroxyl of amorphous silica (denoted hereafter SiOH) and the closely related bridged hydroxyl in H-mordenite [denoted hereafter Si(Al)OH]. The study has been carried out at relatively high temperatures (77 K) and low pressures, to avoid

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