Far-Infrared Laser Spectroscopy of van der Waals Bonds: A Powerful New Probe of Intermolecular Forces

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"Molecular mechanics"—large-scale computer modeling of molecular structure and function—has become one of the most rapidly expanding activities in chemistry and biology. As increasing numbers of scientists turn to these semiempirical computer codes in order to design new drugs, catalysts, artificial enzymes, etc., our incomplete knowledge of the "weak interactions" of chemistry—van der Waals forces and hydrogen bonding (collectively termed intermolecular forces in this article)—is becoming a progressively more serious impediment. Intermolecular potentials are a critical part of the "input" required for molecular mechanics codes, as well as for statistical mechanics and molecular dynamics models of chemical reactions in liquids, gas–surface interactions, and protein dynamics. Even the best such calculations are based on simplistic "6–12 type" forms for the intermolecular potential surfaces (i.e., with isotropic well depths and an average van der Waals distance), usually incorporating the additional assumption of pairwise additivity of intermolecular forces, i.e., neglecting three-body and higher terms in the potential.

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In fact, such relatively crude isotropic potential functions are essentially all that are currently available for the description of intermolecular forces, with the exception of a few simple systems. This reflects the capabilities of the experimental techniques through which intermolecular potentials have traditionally been determined. Most systems have been investigated by measurement of "classical" properties, such as gaseous transport properties, virial coefficients, spectroscopic line broadening, and NMR relaxation times. The most elegant and powerful methods employed for this purpose have been molecular beam measurements of differential scattering cross sections. The classical methods clearly involve measurement of isotropically averaged properties which are extracted with rather low precision, making it impossible to establish the orientation dependence of the intermolecular forces. But even the most sophisticated molecular beam scattering techniques are capable of revealing the orientational variation in these forces only rather crudely—through the damping of quantum mechanical oscillations in the scattering cross sections, which are difficult to measure precisely. Unfortunately, theoretical chemistry has thus far been of limited value in producing reliable values for anisotropic interactions in weakly bound systems. The problem is simply that intermolecular forces can be meaningfully described only with extremely high levels of correlation in an ab initio calculation, and this level of sophistication has remained beyond the capabilities of quantum chemistry for all but the simplest of systems.

Far from being a subtle correction, the anisotropy in intermolecular forces is a dominant feature in many systems, most obviously in those involving hydrogen bonding. A substantial body of knowledge regarding anisotropic intermolecular forces, as deduced from the

vibrationally averaged structures of weakly bound binary complexes, has been assembled from microwave rotational spectroscopy and molecular beam electric resonance experiments (MBER), a field pioneered by Klemperer and his co-workers. For example, Dyke, Howard, and Klemperer's elegant MBER study of the hydrogen fluoride dimer—a prototypical hydrogen-bonded system—revealed an L-shaped structure with a slightly nonlinear (F⋯H–F) hydrogen bond and with rapid quantum tunneling exchanging the roles of the free and H-bonded hydrogens.[1] This type of structural and dynamical information is now available for a large and rapidly growing number of weakly bound systems;[2] however, extraction of global features of the intermolecular potential surfaces from rotational spectroscopy measurements is not possible, since they typically sample only regions near the absolute minimum of the surface.

An impressive array of mid-IR laser rovibrational spectroscopy experiments have also been carried out for binary and some ternary van der Waals complexes.[3] These studies similarly produce valuable information on the structures of complexes and additionally offer the possibility for examining the dynamics of vibrational predissociation, since they involve excitation of high-frequency vibrations of the chemically bonded constituents, which are typically an order of magnitude higher in energy than the binding energy of the complexes. Once again, however, these IR studies usually sample only regions of the intermolecular potential-energy surface (PES) near the global minimum and thus cannot characterize the actual intermolecular potential surface very extensively. An exception to this general fact occurs when either combination bands or hot bands involving excitation of the low-frequency modes are observed, as in the recent work of Nesbitt and co-workers;[4] however, in the former case, the intermolecular potentials corresponding to vibrationally excited monomers are sampled—not their ground states, which is what one generally seeks to characterize.

The theoretical apparatus for inverting these types of data to obtain anisotropic intermolecular potential surfaces (IPS) is well established for only the simplest systems (e.g., atom–diatom). For example, Hutson and Howard[5] have carried out a series of detailed studies of the IPS for the rare gas–hydrogen halide systems, obtained by fitting all available data to analytical forms for the potential and employing numerical integration of the Schroedinger equation ("close coupling") to calculate the bound states of the intermolecular potential. Their results for ArHCl are shown in Figure 1. In this case, the data set included second virial coefficients, HCl line broadening cross sections, rotational constants from MBER spectroscopy, and molecular beam differential scattering cross sections. All of these results could be fit with equally good residuals to a surface only with a single minimum at the linear ArHCl geometry ($\theta = 0$), or to a very different surface
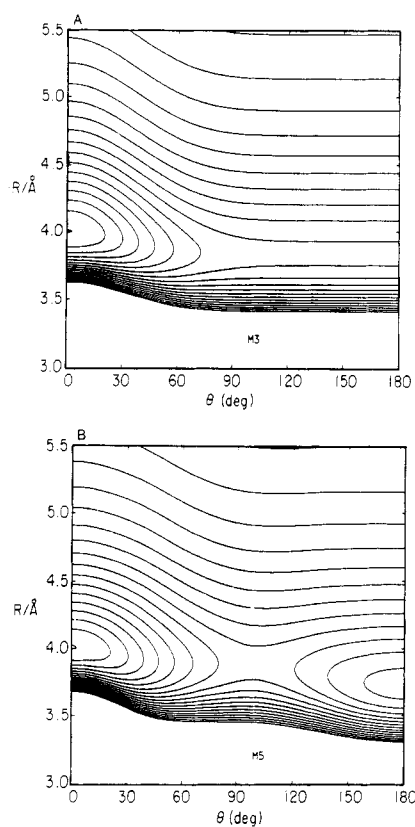

Figure 1. (A) The single-well (M3) potential surface for ArHCl and (B) the double-well (M5) surface obtained by fitting data from microwave spectroscopy, molecular beam scattering, spectral line broadening, and virial coefficient measurements (taken from ref 5). R is the vector joining Ar and the HCl center of mass; θ is the angle between R and the HCl bond axis. Reprinted with permission from ref 5. Copyright 1982 and 1981 Taylor and Francis, LTD.

also having a secondary minimum at the linear ArClH geometry ($\theta = 180°$) and a saddle point near the T-shaped geometry ($\theta = 90°$). The fact that either of these two surfaces, having dramatically different topologies, can fit all these data equally well confirms the notion that the methods used to obtain them are not capable of characterizing intermolecular potential surfaces over the whole range of angles.

A dramatically more accurate and extensive characterization of IPS could be obtained if one were to determine sufficient numbers of the rovibrational eigenstates of the intermolecular potential ("van der Waals vibrations") by precisely measuring their associated spectra and then invert this data to obtain the IPS. However, the weak bonds in neutral van der Waals complexes are usually only 10^{-2}–10^{-3} times as strong as normal chemical bonds (typically 0.1–5 kcal/mol); hence their characteristic vibrational frequencies occur in the far-infrared (far-IR) portion of the spectrum (10–350 cm^{-1}), one of its technologically most inaccessible regions. A plot of the lowest few intermolecular vibrational states of ArHCl, calculated from a double-well potential similar to that of Figure 1B, is given in Figure 2. Some earlier attempts were made to measure transitions among these states, using "conventional" Fourier-transform far-IR spectrometers and cold ambient gas samples.[6] In that work, weak

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(2) Novick, S. E.; Leopold, K. R.; Klemperer, W. *Atomic and Molecular Clusters*; Bernstein, E., Ed.; Elsevier: 1989.

(3) *Structure and Dynamics of Weakly Bound Molecular Complexes*; Weber A., Ed.; D. Reidel Co.: Dordrecht, 1987.

(4) Nesbitt, D. J. *Chem. Rev.* **1988**, *88*, 843.

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(6) Boom, E. W.; Frenkel, D.; van der Elsken, J. *J. Chem. Phys.* **1976**, *66*, 1826; **1982**, *77*, 625.
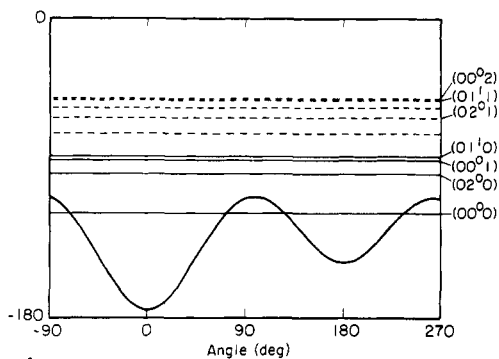
Figure 2. Intermolecular vibrational energy levels of ArHCl. The energies (including zero-point energy of the intermolecular stretching vibration) of the lowest nine states shown are the results of close coupling calculations on the M6B potential surface (ref 13). Solid lines indicate states that have been accessed spectroscopically. The surface shown is a cross section of the M6B potential taken at the value of R that minimizes the energy for each angle. Levels are labeled on the right with standard linear molecule notation.
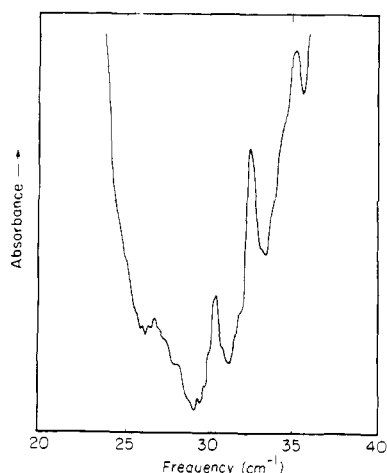

Figure 3. Low-resolution far-IR spectrum of an ArHCl gas mixture obtained in a cold cell, showing features due to intermolecular vibrations in between the HCl rotational lines (from ref 6). Reprinted with permission from ref 6. Copyright 1976 American Institute of Physics.

Figure 4. The P(3) line of the Σ bending vibration–rotation spectrum of ArHCl measured in a planar supersonic jet near 24 cm^{-1} with the Berkeley tunable far-IR laser spectrometer. Reprinted with permission from ref 7. Copyright 1988 American Institute of Physics.

features that could be attributed to stretching and bending modes of the ArHCl complex were visible in between the HCl monomer pure rotational lines (see Figure 3). However, because no rotational structure was observed, a definitive assignment of these far-IR bands could not be made, and very little useful information on the intermolecular PES could actually be extracted.

Demonstrating the current state of the art, Figure 4 displays a spectrum recently obtained at Berkeley for the ArHCl system in this same region ($\sim$24 cm^{-1}) with the use of a newly developed tunable far-IR laser spectrometer.[7] An increase of $\sim$10^3 in sensitivity and of $\sim$10^5 in resolution has been achieved relative to the gas cell experiment by generating molecular complexes at very low temperatures in a continuous planar supersonic jet and measuring their vibration–rotation spectra in direct absorption with a very stable, monochromatic laser source. The dramatically improved sensitivity and resolution that can be obtained with
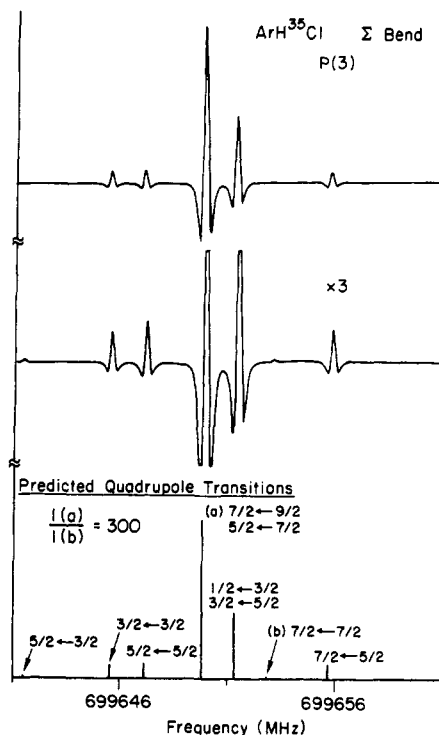
modern laser experiments now make it possible to actually carry out the scenario described above, viz., to precisely measure the low-frequency vibrations of the intermolecular bonds and to invert such data to obtain detailed intermolecular potential surfaces.

The first application of far-IR laser spectroscopy for measurement of intermolecular vibrations was made in 1985 by Marshall et al.[8] They employed MBER detection to measure both direct far-IR and far-IR–microwave double resonance transitions to the lowest Π bending state of ArHCl, near 34 cm^{-1}. The vibrational band origin, rotational constant, *l*-type doubling constant, and the dipole moment of the Π bending state were extracted from five hyperfine Stark components in this pioneering work, but the low sensitivity of the method precluded a more extensive analysis or extension to other vibrational states.

Shortly afterward, Ray et al.[9] reported the measurement of the Π bending spectrum of ArHCl in direct absorption, made by employing electric-field tuning of vibration–rotation transitions in complexes generated in a supersonic jet located inside the cavity of a far-IR laser. A diagram of this experiment is given in Figure 5. The far-IR molecular gas laser is pumped by a CO$_2$ laser. Optical pumping of $\sim$60 different molecules in this way can produce far-IR lasing action at over 2000 different frequencies from 10 to 200 cm^{-1}. The optical cavity is a two-element Fabry-Perot which is adjusted to operate on a single longitudinal mode. Because the laser is not continuously tunable, an electric field is employed to shift molecular transitions into resonance

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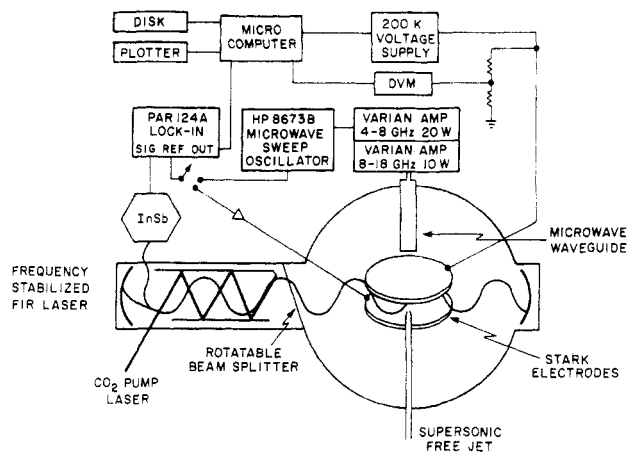298 *Acc. Chem. Res., Vol. 22, No. 9, 1989*

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Figure 5. Schematic diagram of Berkeley far-IR laser Stark spectrometer used to measure van der Waals vibration–rotation spectra in direct absorption. Reprinted with permission from ref 12. Copyright 1988 American Institute of Physics.

with the laser frequency. Detection of the total intracavity power is accomplished by coupling a small fraction of it into an InSb hot electron bolometer. Modulation of the electric field at 100 kHz combined with lock-in detection yields first-derivative line shapes. The supersonic jet is simply a length of $1/4$ in. Pyrex tube, the tip of which is drawn out to an ~ 50 μm orifice. A mixture of $\sim 3\%$ HCl in Ar is expanded from a pressure of ~ 3 atm into the vacuum established by a 10-in. diffusion pump. A scan of the total intracavity laser power versus electric field constitutes the observed spectrum.

Figure 6A shows a single Stark component of the P(1) line of the Π bending vibration, with incomplete resolution of the electric quadrupole hyperfine structure induced by the ^{35}Cl nucleus. The signal-to-noise ratio in this scan exceeds 10^4! Figure 6B shows the same scan, with conditions adjusted for observations of the "inverse Lamb dip" saturation features, resulting from inducing the transitions with a standing wave radiation field. This effects sub-Doppler resolution, at the expense of some loss of sensitivity, and permits complete resolution of the Cl hyperfine splittings.

While a large number of rotational Stark hyperfine lines were measured in this way and analyzed to obtain a detailed characterization of the Π bending state, assignment of these spectra was very tedious and time consuming. Robinson et al.[10] greatly facilitated this process by incorporating microwave double resonance capabilities into the far-IR laser Stark experiment. With this added feature, we could take direct advantage of the extensive microwave results that exist for weakly bound complexes and easily obtained unambiguous assignments of the far-IR rovibronic spectra.

With this combination of far-IR direct absorption and microwave double resonance, additional rovibrational spectra were measured and assigned for both the lowest Σ bending state[10,11] (which correlates with $v = 2$ of the bending mode in the rigid molecule limit) and the lowest van der Waals stretching vibration.[12] Hence, an

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(12) Robinson, R. L.; Ray, D.; Gwo, Dz.-H.; Saykally, R. J. *J. Chem. Phys.* **1988**, *87*, 5149.
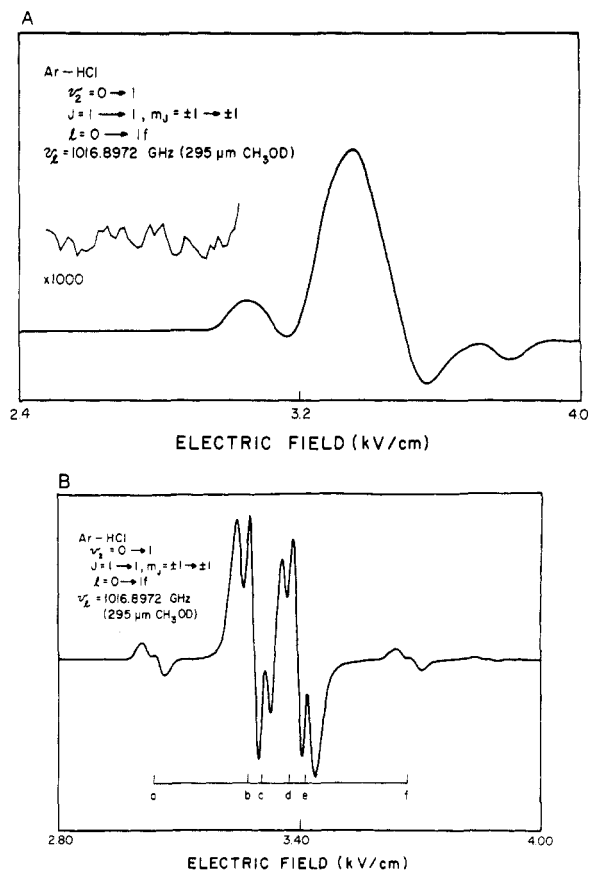

Figure 6. Far-IR laser Stark spectra of Π bending vibration of ArHCl, (A) high-sensitivity mode, (B) high-resolution (Lamb dip) mode, showing hyperfine resolution. Reprinted with permission from ref 9. Copyright 1986 American Institute of Physics.
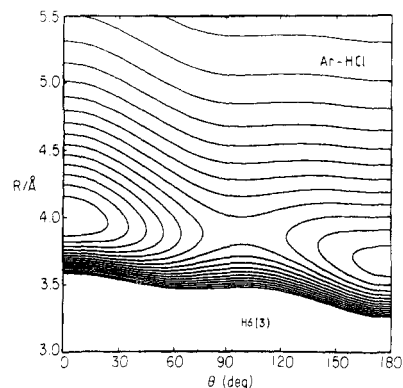

Figure 7. New ArHCl potential surface obtained by J. M. Hutson exclusively from high-resolution spectroscopy data (from ref 13), clearly exhibiting two potential minima. Reprinted with permission from ref 13. Copyright 1988 American Institute of Physics.

extensive data set was obtained for the lowest three intermolecular excited vibrations of ArHCl, including accurate values for vibrational band origins, rotational constants, dipole moments, nuclear quadrupole hyperfine interactions, and Coriolis coupling constants. The dipole moments and hyperfine parameters are particularly significant because they provide direct structural information (the average bending angle) for the complex.

J. M. Hutson[13] has fit these data to an analytical form for the potential surface, using close-coupling methods to integrate the radial part of the Schroedinger equa-

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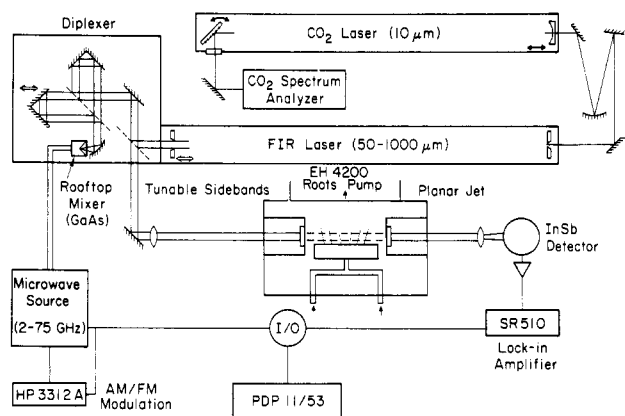
Figure 8. Schematic diagram of Berkeley tunable far-IR laser spectrometer. Reprinted with permission from ref 15. Copyright 1988 American Institute of Physics.

tion. His surface (labeled H6(3)), shown in Figure 7, can reproduce all known measurements on the ArHCl system to within experimental error. It is qualitatively similar to the M5 surface in that it possesses a secondary minimum at the ArClH geometry, but the barrier height is somewhat lower and the secondary minimum is significantly deeper. This demonstrates that by accurately measuring a few of the low-frequency, large-amplitude van der Waals vibrations of a weakly bound complex, an accurate intermolecular PES can be obtained for the system, assuming that the necessary mathematical apparatus required for inversion of the data exists. This approach should be generalizable to a large number of weakly bound systems.

In the last year, we have advanced the experimental approach to the measurement of intermolecular vibrations quite substantially by developing tunable far-infrared laser absorption spectroscopy of weakly bound complexes generated in planar supersonic expansions. This results in narrower line widths and consequent higher precision (1 part in 10^7) as well as a much greater degree of generality. The spectrum of the Σ bend of ArHCl, shown in Figure 4, is representative of the quality of the data that can now be obtained in this manner.

A schematic diagram of the Berkeley tunable far-infrared laser/planar jet spectrometer is shown in Figure 8. This design follows that given by Pickett and his co-workers[14] quite closely. The output from a line-tunable far-IR laser, pumped by a 150-W CO_2 laser, is mixed with frequency-tunable microwave radiation in a Schottky barrier diode, and the tunable sum and difference sidebands are used for spectroscopy. The difficult aspects of this experiment are (i) production of sufficient power in the sidebands to permit sensitive absorption measurements and (ii) separation of the much stronger ($\times 100$–1000) laser carrier radiation from the tunable sidebands, currently accomplished with a polarizing Michelson interferometer. This spectrometer currently can produce single sideband powers as high as 100 μW over the range 10–100 cm^{-1}, permitting fractional absorptions as small as 1 part in 10^6 to be detected. The planar supersonic jet, described in ref 7, effects line widths near 300 kHz and rotational tem-
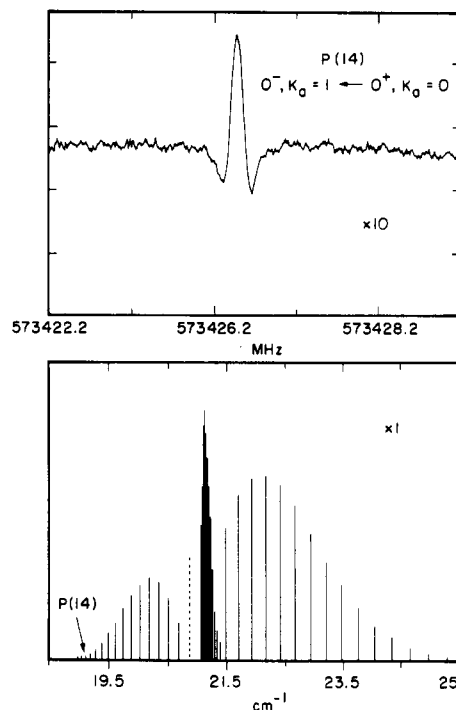

Figure 9. Tunable far-IR laser spectra of assigned vibration–rotation–tunneling (VRT) transitions of the ArH$_2$O complex observed in a planar supersonic jet. Reprinted with permission from ref 15. Copyright 1988 American Institute of Physics.
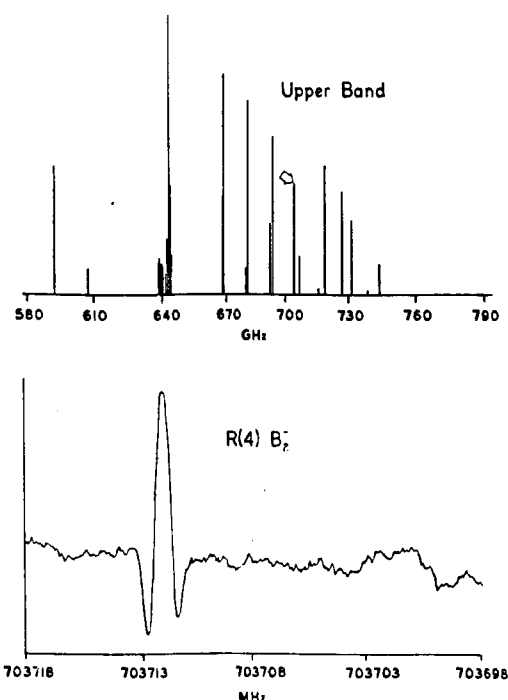

Figure 10. Tunable far-IR laser spectra of rotation–tunneling transitions assigned to the water dimer generated in a planar supersonic jet. Reprinted with permission from ref 17. Copyright 1989 American Institute of Physics.

peratures near 5 K for complexes generated in argon.

This spectrometer has recently been used to measure vibration–rotation–tunneling (VRT) spectra of ArH$_2$O,[15] (HCl)$_2$,[16] (H$_2$O)$_2$,[17] (NH$_3$)$_2$,[18] and ArNH$_3$[19] complexes.

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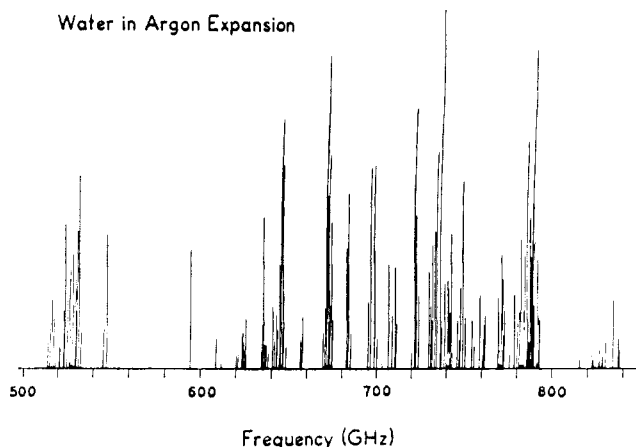
Water in Argon Expansion

Figure 11. A computer plot of all assigned tunable far-IR laser spectra of the water dimer observed near 660 GHz (22 cm⁻¹), as well as unassigned lines found near 780 GHz (26 cm⁻¹), probably due to higher clusters.

Representative spectra of ArH_2O and $(H_2O)_2$ taken over the range 20–30 cm⁻¹ are shown in Figures 9 and 10, respectively. In Figure 11, a stick spectrum of the lines observed in an Ar–H_2O expansion (after those of the Ar–H_2O complex have been subtracted) is given. Of particular interest are the transitions observed near 22 cm⁻¹ assigned to the water dimer, and those (unassigned) near 26 cm⁻¹, due to higher argon–water clusters.

Our objective in these studies is to provide a detailed characterization of the structures and internal dynamics of these weakly bound complexes as the requisite first step toward the ultimate goal: obtaining detailed three-dimensional intermolecular potential-energy surfaces for molecular "weak interactions". The current state of the art limits us to studies of binary systems, but several groups are currently seeking to extend both the theory and experiments to address ternary and quaternary complexes. This will afford a detailed examination of the many-body effects (e.g., Axelrod–Teller "triple dipole" dispersion interaction), which becomes of potential importance in models of the chemistry of liquids.

The investigation of intermolecular forces has entered a new era. The first-generation experiments in this field involved measurement of bulk gaseous properties (diffusion, virial coefficients, etc.), and the results obtained (viz., "6-12" potentials) are described in the classic work of Hirschfelder, Curtiss, and Bird, "The Molecular Theory of Gases and Liquids",[20] published in 1954. The second era was initiated by much more detailed molecular beam differential scattering studies, which required more sophisticated forms for the intermolecular potentials. Still, most of these studies involved rare-gas atoms and only isotropic models of molecular interactions. A summary of these results is available in the text by Maitland, Rigby, Smith, and Wakeham, "Intermolecular Forces—Their Origins and Determinations",[21] revised and published in 1987. The quality of information available in the current era is represented by the new ArHCl potential surface presented in Figure 7, obtained exclusively from high-resolution spectroscopy. The study of intermolecular forces through precise measurement of van der Waals vibration–rotation–tunneling spectra with far-infrared laser methods and inversion of these data by sophisticated numerical analysis methods can now produce highly detailed anisotropic surfaces with unprecedented accuracy. Recently, Dykstra and co-workers[22] have developed an interesting new ab initio route to intermolecular forces which appears to be accurate and quite general. We can anticipate qualitative advances in our understanding of van der Waals forces and hydrogen bonding and their effects on condensed-phase behavior and molecular dynamics to result, as both theory and experiment continue to address sequentially more complex systems.

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