Structure, Dynamics, and Thermodynamics of Clusters: Tales from Topographic Potential Surfaces

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Theoretical studies of atomic and molecular clusters often seek to explain structure, dynamics, and thermodynamics in terms of the underlying potential energy surface and the form of the interparticle interaction. One specific example from each of these categories is considered here; the overall approach can be summarized as global analysis of potential surfaces. Changes in the most favorable cluster morphology can be qualitatively understood as a function of the range of the interparticle forces. Thermodynamic properties can be calculated from a representative sample of local minima on the potential energy surface. However, prediction of dynamics requires not only knowledge of minima but also transition states and reaction pathways.

The potential energy surface and the interatomic or intermolecular potentials from which it is constructed play a fundamental role in providing a detailed understanding of the structure, dynamics, and thermodynamics of clusters. The most important features that arise on any cluster potential energy surface are familiar objects in three-dimensional space but are rather harder to visualize in hundreds of dimensions. Local minima in the potential energy surface correspond to basins in a mountain range. At the bottom of a basin, the only way to walk is uphill, and any sufficiently small structural perturbation of a local minimum on a potential energy surface similarly causes an increase in the potential energy. Local energy minima are one kind of stationary point on the surface, where all the forces vanish. They are locally stable, in that any infinitesimal change of structure raises the energy. A transition state, on the other hand, corresponds to the highest point along the valley linking two basins. Transition states are also stationary points, but correspond to mechanical instability: infinitesimal displacements in either direction along the reaction path lower the energy.

Unfortunately, the high dimensionality of the nuclear configuration space for a cluster means that the number of minima and transition states on the potential energy surface can be astronomically large. In fact, the number of structurally distinct minima is thought to grow exponentially with the number of atoms in the cluster (1, 2). This difficulty has important consequences for theoretical studies of all aspects of cluster science. Perhaps the most fundamental question that one can address is the identity of the lowest energy minimum. This problem immediately takes us into the domain of global optimization theory and is only readily answered for surfaces that

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possess "funneling" properties (3), where searches are more likely to lead to the global minimum. In particular, it appears that the location of the global minimum is an "NP-hard" problem (4), which means that no algorithm can be found that scales as a polynomial in the number of atoms; instead, the best that one can achieve is an algorithm that scales exponentially.

The exponential increase of the number of minima and the likely time required to find the lowest minimum as a function of the number of atoms might appear rather discouraging. However, cluster science may soon provide insight into fields such as protein folding, where Levinthal's "paradox" celebrates the fact that a random search for the native state of a protein is incompatible with experiment (5). Recent insights have come from studies of clusters bound by simple analytical potentials, where thousands of minima and transition states can be located in a reasonable amount of computer time (6). Empirical potentials provide closed-form expressions for the energy of a system in terms of interatomic distances and perhaps angles. Hence, they also define the interatomic force law through first derivatives of the energy with respect to coordinates. Although the simplest model potentials may only be realistic for systems such as inert gas clusters, the experience gained in handling such databases has already borne fruit (7). In this article, specific examples for three important aspects of cluster science, namely structure, dynamics, and thermodynamics, are discussed, with particular emphasis on how the underlying potential energy surface can provide a unifying framework to explain the phenomena observed.

Structure—The Range of the Potential

For a simple interatomic potential with a single adjustable parameter designed to represent some particular bonding characteris-

tic, it is possible to understand in some detail how the favorable cluster morphology changes with both the value of the parameter and the size of the cluster. Here we consider clusters bound by the Morse potential (8), a simple pair potential that contains one variable parameter which may be used to change the range of the interparticle force (9, 10). Of course, in adapting such a functional form, it is assumed that the energy is pairwise additive, and possible many-body terms and anisotropy are neglected. Nevertheless, calculations such as these help to disentangle such effects and can produce useful qualitative insights in their own right.

The lowest energy morphology for clusters bound by pairwise-additive, isotropic forces is determined by a balance between the total number of nearest-neighbor interactions (stabilizing) and the strain energy (destabilizing). The latter quantity reflects the deviation of nearest-neighbor contacts from their most favorable value (10) (and must not be confused with bulk strain as applied to bulk systems in the context of elastic constants). Aside from very long range potentials, the lowest energy structure is generally based on one of three different morphologies (10): Mackay icosahedra (11), decahedra, and close-packed fragments of regular bulk lattice. Mackay icosahedra (Fig. 1A) can be constructed from 20 distorted tetrahedral segments—one corresponding to each face of the icosahedron—sharing a common vertex in the center of the cluster. The 20 surface facets are all essentially close-packed. A pentagonal bipyramid with a single fivefold axis can be constructed from five distorted tetrahedra sharing an edge, which corresponds to the principal axis (12). Lower energy decahedra can be formed if the pentagonal bipyramid is truncated (13); the Marks decahedron with re-entrant {111}-type faces is probably the most favorable (Fig. 1B). In clusters, the lowest energy structures based on close-packing can be constructed either from truncated octahedra or tetrahedra (10) (Fig. 1C). The close-packed geometries are essentially strain free but expose some surface facets that are not close-packed.

Of the three morphologies, the icosahedron maximizes the number of nearest-neighbor contacts but has the highest strain, the truncated octahedron minimizes the strain but has the fewest nearest-

neighbor contacts, and the Marks decahedron is intermediate in both categories. Direct comparisons between these structures are not straightforward because complete geometries of high symmetry, which are expected to be particularly low in energy, occur for different numbers of atoms (Fig. 1). Hence, for clusters containing less than around 100 atoms, the most stable morphology may change with the addition or removal of a single atom.

Results obtained with the Morse potential show that the strain energy generally increases for a given morphology with increasing size and for shorter range potentials (10). Hence, as either the size increases or the range decreases, the morphology of the global minimum changes from icosahedral to decahedral to close-packed. Qualitatively, this observation suggests several immediate applications. Because the intermolecular C_{60} potential used in a number of previous studies (14) has a very short effective range, one would expect to see "magic numbers" for neutral C_{60} clusters corresponding to decahedral or close-packing. Experiments with charged C_{60} clusters exhibit magic numbers characteristic of Mackay icosahedra (15), where longer ranged forces may be present. Experiments with neutral clusters, which will effectively act as a check on the intermolecular potential used, are eagerly awaited. Recent simulations of bulk C_{60} suggest that the liquid phase has only a narrow range of stability (16) or none at all (17). An atomic basis for the instability of the liquid phase has recently been suggested (18), again based on considerations of strain energy in the liquid and solid phases. This theory is consistent with results from colloid studies, where the effective range of the potential can be varied systematically (19).

Temperature-dependent spectra of sodium clusters have been interpreted in terms of electronic magic numbers for warm, liquidlike clusters and geometrical magic numbers for cold, solidlike clusters (20). The effective interatomic potential in this case probably has a much longer range, meaning that there are likely to be a large number of highly strained and disordered but low-energy minima (10). A low melting temperature is expected with such a potential energy surface. Furthermore, because strain can be accommodated with little energetic penalty, the system can probably adopt a geometry that optimizes the electronic energy. Hence, once the temperature is high enough for the most electronically favorable structures to be accessed, electronic magic numbers are expected, in agreement with experiment.

Clusters composed of small molecules often exhibit bulklike packing schemes at much smaller sizes than atomic clusters (21). The rapid convergence of molecular clusters composed of species such as CCl_4 and SF_6 to bulklike phases might therefore be the result of intermolecular potentials with a range that is short compared with the pair separation at equilibrium, because the strain energy for a given morphology increases with size. However, this interpretation is complicated by the anisotropic nature of the intermolecular forces and the fact that the corresponding bulk phases are not generally cubic close-packed.

Insight into cluster structure can therefore sometimes be gained from relatively simple potentials, complementing more accurate studies of specific systems, which may involve detailed quantum mechanical calculations (22). However, to understand thermodynamic properties it is necessary to consider local minima on a potential energy surface other than the lowest, because these may be populated at finite temperatures. In the next section, we
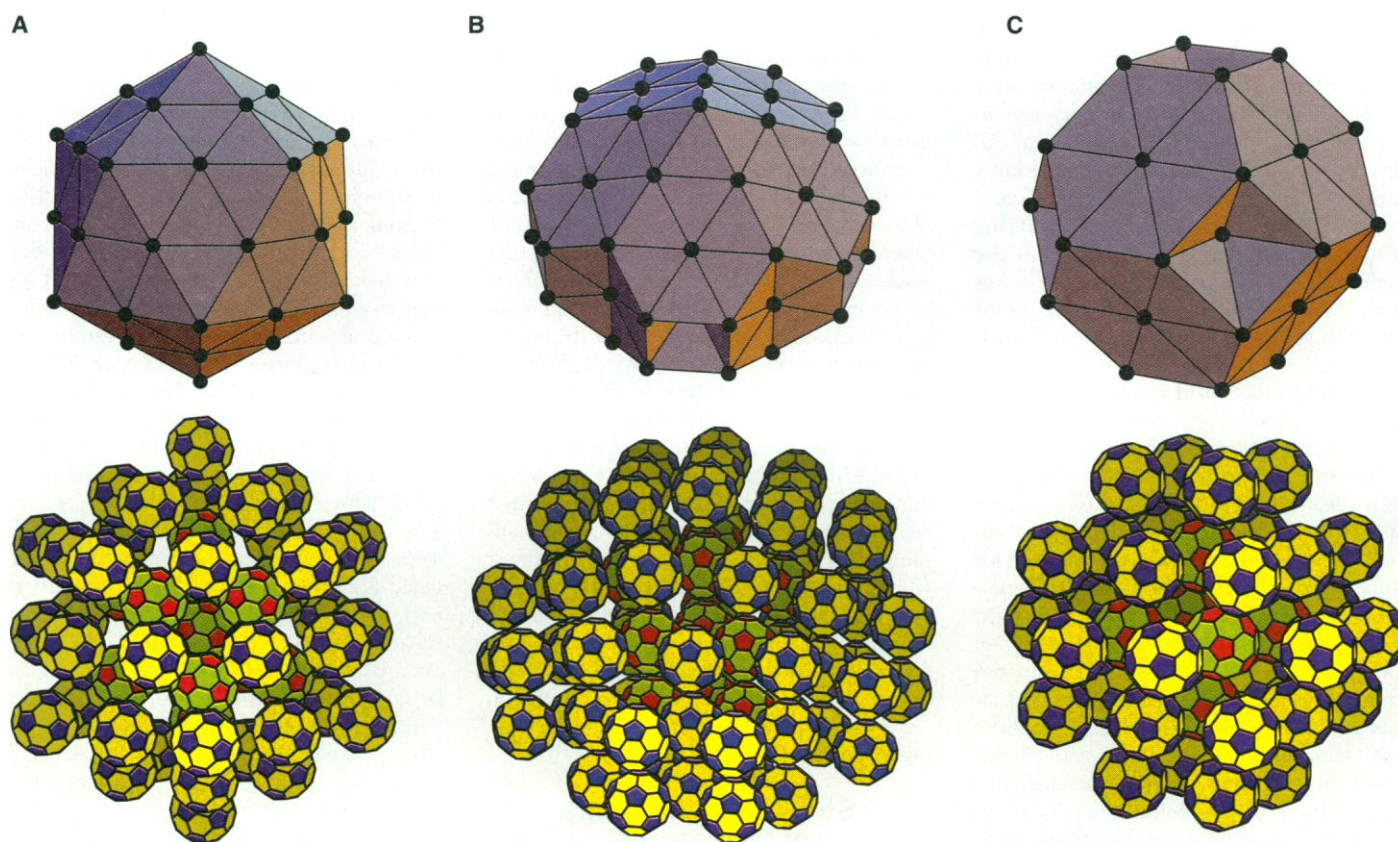
Fig. 1. Candidate morphologies for the global minimum of a small cluster. In each case, a triangulated representation designed to give an impression of the overall shape is shown (top) along with a realization of the structure for a cluster of C_{60} molecules (bottom). (**A**) Mackay icosahedron containing 55 particles. (**B**) Marks decahedron containing 75 particles. (**C**) Truncated octahedron with regular hexagonal faces containing 38 particles. Graphics produced with Mathematica (45).

show how thermodynamic properties can be deduced from large, representative samples of minima (23, 24). Such calculations represent an approximate global analysis of the potential energy surface (7, 25).

Thermodynamics—Peculiarities of Small Systems

Finite systems can exhibit thermodynamic properties that are rigorously forbidden in bulk material. For example, if energy can be added in a controlled fashion to an isolated cluster, then it is possible for the internal temperature to fall as the energy is increased. This behavior corresponds to a negative heat capacity and has been characterized in numerous computer simulations. An experimental realization of this hypothetical procedure would correspond to absorption of single photons by a cluster in a collision-free molecular beam.

The general conditions under which such behavior is possible are now well understood in terms of thermodynamic distributions (26) and are also inherent in much earlier work by Hill (27). In bulk material, the first-order melting transition is characterized by solid and liquid phases in contact at the melting point. However, for small systems the energetic penalty for forming an interface is too large for such phase separation to be observed. Instead, it is helpful to think of an isolated individual cluster in terms of a two-state model (28–30) where in the melting region the cluster is at times solidlike and at times liquidlike. A dynamic equilibrium exists between the two forms with an equilibrium constant that is related to the difference in free energy. If the temperature of the cluster rather than its total energy is under experimental control, the heat capacity has to be positive (29, 31).

Accurate calculations of thermodynamic properties for clusters have now demonstrated the above effects beyond reasonable doubt (32). However, further insight can be gained from approximate calculations in which the same quantities are calculated from a distribution of local minima on the potential energy surface (23, 24). A similar viewpoint has been exploited by Stillinger and Weber in their studies of bulk melting (2). The objective is to partition the separate contributions to thermodynamic functions of different regions of phase space corresponding to solidlike and liquidlike clusters, and to achieve this, we need a suitable "order parameter" that tells us which region we are in. A qualitative understanding of this procedure in terms of the two-state model is not difficult. Solidlike regions of phase space are associated with restricted motion in low-energy minima. In contrast, liquid-

like regions of phase space are associated with passage between a multitude of higher energy, disordered minima (33). For an isolated cluster at constant total energy, the kinetic energy is larger when the system is associated with a low-energy, solidlike minimum and smaller when it visits liquidlike regions of phase space with higher potential energy. When the total energy is small, the system simply vibrates in a particular low-lying potential well. As the energy rises, the amplitude of the vibrations increases until eventually the cluster can escape to regions of the potential energy surface that correspond to liquidlike behavior. However, the mean kinetic energy, and hence our measure of the internal temperature, can decrease when this happens.

In a particular model of the rare gas cluster Ar_{55}, the potential energy of minima associated with solidlike and liquidlike phase space is sufficiently different to act as an order parameter in identifying which region is which (24). The (Helmholtz) free energy A can then be calculated as a function of potential energy V and temperature T (Fig. 2A). Two valleys in the surface, separated by a ridge and corresponding to the solidlike and liquidlike forms, coexist over a well-defined temperature range. A cross section of the surface taken at a temperature in the coexistence region reveals two free energy wells (Fig. 2B). The well corresponding to the solidlike "phase" is associated with the Mackay icosahedral global minimum (Fig. 1A) and defective icosahedra, whereas the well corresponding to the liquidlike "phase" is associated with all the other generally amorphous minima (24).

Such calculations provide fundamental insights, but direct comparison with experiments is difficult. However, applications to calculation of nucleation rates, for example, are likely to be of future interest. The next logical step, having considered cluster thermodynamics in terms of distributions of minima, is to investigate global dynamics in terms of distributions of transition states. The first efforts in this direction for clusters containing more than 10 atoms have recently appeared (7, 25). For smaller systems with relatively few local minima, significant progress has already been made. In the next section, we focus on small water clusters, for which splittings resulting from quantum tunneling have been accurately measured and understanding has been gained as a result of close interaction between theory and experiment.

## Dynamics—Tunneling in Small Water Clusters

The application of far-infrared vibration-rotation tunneling spectroscopy (34) to small water clusters (35–37) has recently led to a

flurry of both theoretical and experimental activity (38). Here the water trimer is used to show how a global view of the potential energy surface is needed to understand the splittings in the vibration-rotation energy levels that result from rearrangements of the hydrogen-bonding network.

If imaginary labels are attached to all of the atoms in a given structure, then it is possible to distinguish permutational isomers that correspond to distinct minima on the potential energy surface. To a first approximation, each of these minima supports an identical set of localized wave functions corresponding to vibrational and rotational degrees of freedom. However, there may exist rearrangements between different permutational isomers that result in these min-
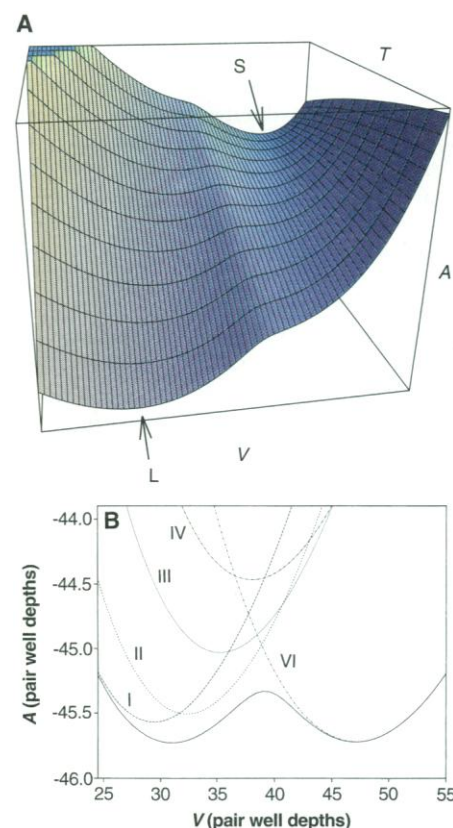
Fig. 2. (A) Free energy surface (A) for Ar_{55} as a function of temperature T and potential energy V, calculated with a distribution of local minima. A linear term in T has been added to highlight the solidlike (S) and liquidlike (L) wells. **(B)** Contribution of solidlike and liquidlike regions of the potential energy surface to the free energy A as a function of potential energy V, calculated at the temperature corresponding to the middle of the coexistence region in (A). Curve I corresponds to the global minimum Mackay icosahedron (Fig. 1A), curves II through IV correspond to increasingly defective Mackay icosahedra, and curve VI corresponds to contributions from minima associated with liquidlike regions of phase space (24). Both A and V are measured in units of energy equal to the pair well depth, that is, the depth of the potential well at its lowest point for a single pair of atoms or molecules.
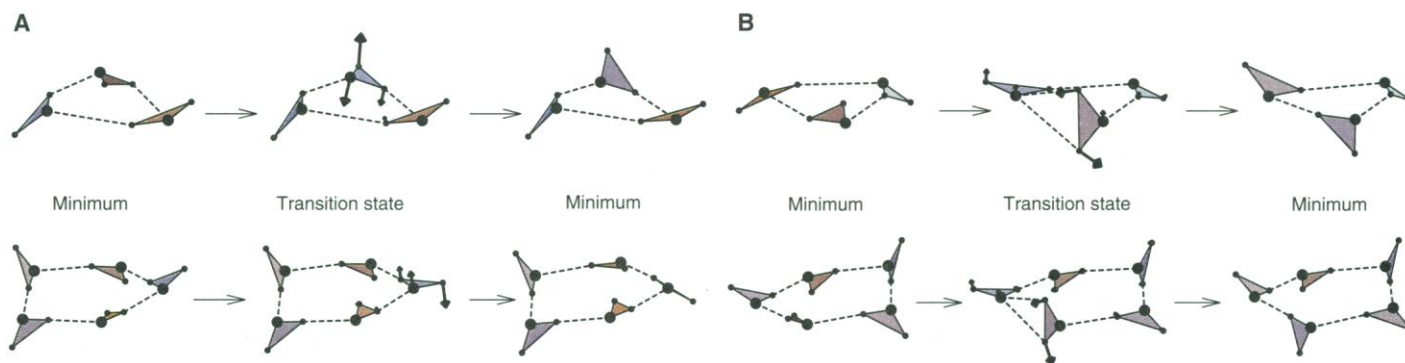
Fig. 3. Low-energy rearrangements of $(H_2O)_3$ (top) and $(H_2O)_5$ (bottom) from ab initio theoretical calculations (40, 41). (**A**) The particularly facile single-flip process. (**B**) Higher energy mechanism involving transition states with "bifur- cated" hydrogen bonds in which one molecule acts as a double donor and another as a double acceptor. Graphics generated with Mathematica (45) using a distance cutoff to define the hydrogen bonds.

ima being linked by valleys on the potential energy surface. If the barrier represented by the highest point on each valley is not too large and the length of the pathway is not too long, then interference can occur between the localized states of each minimum. This effect is a result of quantum mechanical tunneling through the energy barriers and leads to splittings of the localized states, which can often be observed spectroscopically. A rearrangement that leads to splittings within the experimental resolution is said to be "feasible" (39).

As shown, a sample of minima can be used to gain insight into cluster thermodynamics, but to interpret tunneling splittings, additional information is needed concerning the rearrangement mechanisms and the transition states that link different minima. Far-infrared vibration-rotation tunneling spectroscopy provides indirect information about these mechanisms and shifts the experimental focus and the challenge to theory from minima to transition states. The tunneling splitting pattern that results when a particular mechanism is feasible can be predicted with a little further computation once the details of the rearrangement are known. Determining the pattern requires the construction of a complete reaction graph consisting of a closed set of permutational isomers linked by the rearrangement and the connections between them. Accurate calculation of the magnitudes of the tunneling splittings is much harder, but it may be possible to assign features in a spectrum to particular mechanisms without these calculations.

Two mechanisms of particularly low energy have been characterized (40) in ab initio calculations for $(H_2O)_3$, and close analogs appear to exist (41) for $(H_2O)_5$. The first is the single "flip" (Fig. 3A), which Pugliano and Saykally postulated would be the most facile rearrangement (35). The second is a process that we will call bifurcation tunneling because the transition state features a "bifurcated" hydro-

gen-bonding pattern (Fig. 3B). It is closely analogous to the donor tunneling rearrangement of the water dimer (36) and entails a significantly larger energy barrier than the single flip (40, 42). When both of these processes are feasible, the resulting tunneling splitting pattern consists of a widely spaced quartet of levels, each of which is further split into another quartet with much smaller spacings (40). The quartets corresponding to the fine structure have been observed experimentally (36) and are caused by the bifurcation tunneling process.

More accurate studies of the restricted potential energy surface and tunneling dynamics associated with the single-flip mechanism have since been presented (43), and one calculation including the bifurcation tunneling dynamics has appeared (44). The results help to quantify the patterns described above and provide further information concerning excited states. Preliminary calculations for $(H_2O)_5$ have identified analogous rearrangement pathways that will result in very complicated splitting patterns if both mechanisms are feasible (41).

Conclusions

This article has emphasized the central role of the potential energy surface in rationalizing the structure, dynamics, and thermodynamics of clusters. Considerable progress has been made in relating the favored low-energy structures to features of the interatomic or intermolecular potential that have clear physical interpretations. For example, geometries based on Mackay icosahedra and close-packing are likely to be favored for long- and short-ranged isotropic potentials, respectively. Insight into the sometimes unfamiliar thermodynamic properties of finite systems can be gained from calculations based on distributions of potential energy minima. However, although an approximate global analysis of the potential energy surface in terms of the minima may be sufficient to

rationalize thermodynamic properties, more detailed information is needed to understand dynamics. Such studies are only just beginning for systems with many degrees of freedom. For small water clusters, theoretical characterization of low-energy rearrangement mechanisms has already helped to interpret the tunneling splittings observed in recent laser spectroscopy experiments. The logical progression to useful approximate treatments of the dynamics in larger systems, such as biomolecules, will have far-reaching consequences.

REFERENCES AND NOTES

1. M. R. Hoare and J. McInnes, *Faraday Discuss. Chem. Soc.* **61**, 12 (1976).
2. F. H. Stillinger and T. A. Weber, *Phys. Rev. A* **25**, 978 (1982).
3. J. D. Bryngelson, J. N. Onuchic, N. D. Socci, P. G. Wolynes, *Proteins* **21**, 167 (1995).
4. L. T. Wille and J. Vennik, *J. Phys. A* **18**, L419 (1985).
5. C. Levinthal, in *Mössbauer Spectroscopy in Biological Systems: Proceedings of a Meeting Held at Allerton House, Monticello, Illinois*, P. DeBrunner, J. Tsibris, E. Munck, Eds. (Univ. of Illinois Press, Urbana-Champaigne, IL, 1969), p. 22.
6. C. J. Tsai and K. D. Jordan, *J. Phys. Chem.* **97**, 11227 (1993); D. J. Wales, *J. Chem. Phys.* **101**, 3750 (1994).
7. K. D. Ball *et al.*, *Science* **271**, 963 (1996).
8. P. M. Morse, *Phys. Rev.* **34**, 57 (1929).
9. P. A. Braier, R. S. Berry, D. J. Wales, *J. Chem. Phys.* **93**, 8745 (1990).
10. J. P. K. Doye, D. J. Wales, R. S. Berry, *ibid.* **103**, 4234 (1995).
11. A. L. Mackay, *Acta Crystallogr.* **15**, 916 (1962).
12. B. G. Bagley, *Nature* **208**, 674 (1965).
13. S. Ino, *J. Phys. Soc. Jpn.* **27**, 941 (1969); L. D. Marks, *Philos. Mag. A* **49**, 81 (1984).
14. L. A. Girifalco, *J. Phys. Chem.* **96**, 858 (1992).
15. T. P. Martin, U. Näher, H. Schaber, U. Zimmermann, *Phys. Rev. Lett.* **70**, 3079 (1993).
16. A. Cheng, M. L. Klein, C. Caccamo, *ibid.* **71**, 1200 (1993).
17. M. H. J. Hagen, E. J. Meijer, G. C. A. M. Mooij, D. Frenkel, H. N. W. Lekkerkerker, *Nature* **365**, 425 (1993).
18. J. P. K. Doye and D. J. Wales, *Science* **271**, 484 (1996).
19. A. P. Gast, C. K. Hall, W. B. Russel, *J. Colloid Interface Sci.* **96**, 251 (1983); E. J. Meijer and D. Frenkel, *J. Chem. Phys.* **100**, 6873 (1994); S. M. Illett, A. Orrock, W. C. K. Poon, P. N. Pusey, *Phys. Rev. E* **51**, 1344 (1995).
20. T. P. Martin, T. Bergmann, H. Göhlich, T. Lange, *Chem. Phys. Lett.* **172**, 209 (1990); T. P. Martin, U.

Näher, H. Schaber, U. Zimmermann, *J. Chem. Phys.* **100**, 2322 (1994).
21. L. S. Bartell, *J. Phys. Chem.* **99**, 1080 (1995).
22. G. Scuseria, *Science* **271**, 942 (1996).
23. D. J. Wales, *Mol. Phys.* **78**, 151 (1993); G. Franke, E. R. Hilf, P. Borrmann, *J. Chem. Phys.* **98**, 3496 (1993).
24. J. P. K. Doye and D. J. Wales, *J. Chem. Phys.* **102**, 9659 (1995); *ibid.*, p. 9673.
25. R. E. Kunz and R. S. Berry, *ibid.* **103**, 1904 (1995).
26. D. J. Wales and R. S. Berry, *Phys. Rev. Lett.* **73**, 2875 (1994); R. M. Lynden-Bell and D. J. Wales, *J. Chem. Phys.* **101**, 1460 (1994); D. J. Wales and J. P. K. Doye, *ibid.* **103**, 3061 (1995).
27. T. L. Hill, *J. Phys. Chem.* **57**, 324 (1953); *J. Chem. Phys.* **23**, 812 (1955).
28. _____, *Thermodynamics of Small Systems: Part I* (Benjamin, New York, 1963).
29. J. D. Honeycutt and H. C. Anderson, *J. Phys. Chem.* **91**, 4950 (1987).
30. R. S. Berry and D. J. Wales, *Phys. Rev. Lett.* **63**, 1156 (1989); D. J. Wales and R. S. Berry, *J. Chem. Phys.* **92**, 4283 (1990).
31. D. Lynden-Bell and R. M. Lynden-Bell, *Mon. Not. R. Astron. Soc.* **181**, 405 (1977); M. Bixon and J. Jortner, *J. Chem. Phys.* **91**, 1631 (1989).
32. P. Labastie and R. L. Whetten, *Phys. Rev. Lett.* **65**, 1567 (1990); H.-P. Cheng, X. Li, R. L. Whetten, R. S. Berry, *Phys. Rev. A* **46**, 791 (1992); S. Weerasinghe and F. G. Amar, *J. Chem. Phys.* **98**, 4967 (1993).
33. R. S. Berry, T. L. Beck, H. L. Davis, J. Jellinek, *Adv. Chem. Phys.* **70**, 75 (1988).
34. R. C. Cohen and R. J. Saykally, *J. Phys. Chem.* **94**, 7991 (1990); N. Pugliano and R. J. Saykally, *J. Chem. Phys.* **96**, 1832 (1992); R. J. Saykally and G. A. Blake, *Science* **259**, 1570 (1993).
35. N. Pugliano and R. J. Saykally, *Science* **257**, 1937 (1992).
36. K. Liu *et al.*, *J. Am. Chem. Soc.* **116**, 3507 (1994).
37. K. Liu *et al.*, *Faraday Discuss. Chem. Soc.* **97**, 35 (1994); S. Suzuki and G. A. Blake, *Chem. Phys. Lett.* **229**, 499 (1994).
38. K. Liu, R. J. Saykally, J. D. Cruzan, *Science* **271**, 929 (1996).
39. H. C. Longuet-Higgins, *Mol. Phys.* **6**, 445 (1963).
40. D. J. Wales, *J. Am. Chem. Soc.* **115**, 11180 (1993).
41. _____, in preparation.
42. J. E. Fowler and H. F. Schaefer, *J. Am. Chem. Soc.* **117**, 446 (1995).
43. M. Schütz, T. Bürgi, S. Leutwyler, H. B. Bürgi, *J. Chem. Phys.* **99**, 5228 (1993); W. Klopper and M. Schütz, *Chem. Phys. Lett.* **237**, 536 (1995); T. Bürgi, S. Graf, S. Leutwyler, W. Klopper, *J. Chem. Phys.* **103**, 1077 (1995); W. Klopper, M. Schütz, H. P. Lüthi, S. Leutwyler, *ibid.*, p. 1085; J. G. C. M. van Duijneveldt–van de Rijdt and F. B. van Duijneveldt, *Chem. Phys. Lett.* **237**, 560 (1995); D. Sabo, Z. Bačić, T. Bürgi, S. Leutwyler, *ibid.* **244**, 283 (1995).
44. J. K. Gregory and D. C. Clary, *J. Chem. Phys.* **102**, 7817 (1995).
45. Mathematica 2.0, Wolfram Research, Champaign, IL; S. Wolfram, *Mathematica* (Addison-Wesley, Redwood City, CA, ed. 2, 1991).
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Water Clusters

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A surge of progress in both laser spectroscopy experiments and theoretical dynamics methods has facilitated new, highly detailed studies of water clusters. The geometrical structures and hydrogen-bond tunneling pathways of the water trimer, tetramer, pentamer, and hexamer systems have recently been characterized with global analysis of potential surfaces, diffusion Monte Carlo calculations, and far-infrared laser vibration-rotâtion tunneling spectroscopy. Results from these and other studies are yielding important insights into the cooperativity effects in hydrogen bonding, aqueous solvation, and hydrogen-bond network rearrangement dynamics, which promise to enhance our understanding of solid and liquid water behavior.

The study of van der Waals clusters is a very active subfield of cluster science (*1*, *2*). Arguably, the most important weakly bound complexes are pure water clusters. They have been directly implicated in several contemporary problems, including the formation of acid rain (*3*), the anomalous absorption of sunlight by clouds (*4*), and the nucleation of water droplets (*5*). Moreover, the use of water clusters in an indirect context offers an exciting prospect for important scientific advances in untangling the molecular details, for example, of aqueous solvation, cooperativity in hydrogen bonding, and hydrogen-bond network rearrangement dynamics that are so prevalent in the behavior of liquid water (*6*). The strong, directional intermolecular bonding and the capacity of water to act both as a double donor and a double acceptor of hydrogen bonds make water clusters less suitable for a rigorous theoretical treatment than other simple, weakly bound systems. Nevertheless, a recent surge of progress both in theory and experiment has made it possible to study water clusters at an un-

precedented level of detail. In this article, we survey some of these developments and the chemical insight that has been gained from them.

Structures of Small Water Clusters

Theory and experiment are in fairly good agreement for the structure of the water dimer, determined spectroscopically in 1977 by Dyke, Mack, and Muenter (*7*). A number of recent high-level ab initio calculations (*8*) have predicted the structures of larger water clusters (Fig. 1). All the calculations predict that a quasi-planar cyclic form with each monomer acting as both a single donor and single acceptor, and with the free hydrogens oriented above and below the ring, constitutes the lowest energy structure for the trimer, tetramer, and pentamer. For the heptamer and larger clusters, a tendency toward three-dimensional (3D) structures is predicted, with the nature of the hexamer structure being ambiguous (*9*). In this evolution of structure with cluster size, the critical feature is the competition between maximizing the number of hydrogen bonds and minimizing the geometrical

strain. The highest level ab initio calculations (*10*) predict a 3D cage structure to be the most stable for the hexamer, although at least three other structures lie within 0.3 kcal/mol and vibrational-averaging effects are likely to change their ordering. Interestingly, the predicted ring forms of the trimer, pentamer, and heptamer have no symmetry elements and are therefore chiral.

Our recent far-infrared laser vibration-rotation tunneling (VRT) spectroscopy experiments (*11*) support the theoretical predictions. For the trimer (*12*), tetramer (*13*), and pentamer (*14*), we found rotational energy level patterns that are rigorously those of a symmetric rotor ($A = B > C$, where A, B, and C are reciprocal moments of inertia, for example, $A = \hbar^2/2I_a$, where $\hbar$ is Planck's constant divided by 2π). In the case of the trimer, we could separately determine precise values for each of the three rotational constants and, therefore, definitively establish that the structure is an oblate symmetric rotor conforming rather closely to the predictions. Moreover, the large observed negative inertial defect ($I_c - I_b - I_a$) testifies to extensive out-of-plane motions by the free hydrogens. As discussed later, it is these large amplitude motions of the free hydrogens, actually a torsional motion of the water monomers about their donor hydrogen-bond axes ("flipping"), that produces the observed symmetric rotor spectrum through vibrational averaging over the totally asymmetric equilibrium structure.

For the tetramer and pentamer, we have not yet been able to extract such complete information. Precise values were deduced for the $A = B$ rotational constants, but the value for C (describing rotation about the symmetry axis) could only be estimated through simulations of the VRT intensity patterns. Nevertheless, the resulting precision was sufficient to unambiguously establish that the struc-

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