favorable equilibrium with the atmospheric reservoir. Formation of a hydrate is but one component of the ocean disposal process, and it can have a dramatic effect.

References and Notes
4. For injections at depths of <1000 m we used the R/V Point Lobos and ROV Ventana. The 3627-m experiment was carried out using the R/V Western Flyer and the ROV Tiburon. The R/V Western Flyer is a 35.7-m SWATH (small waterplane area twin hull) ship with a center “moon pool” for ROV deployment. Tiburon is a 4000-m capable ROV attached to the mother ship by an armored steel cable with both copper power conductors and single-mode optical fibers for communication and control. Six 3.7-kW electric thrusters supply thrust. The vertical ascent speed is 100 m/min (30.48 m/min). The experiments were imaged by the vehicle cameras and data were recorded on videotape. The Ventana observations were made with a Sony DVC-3000 three-chip camera, and the Tiburon made observations with two Panasonic VW E550 three-chip cameras, with data recorded in digital beta format. Ocean temperature, pressure, and conductivity were sensed continuously by a CTD package (Falmouth Scientific) attached to either vehicle within 2 m of the experimental chambers.
10. Liquid CO2 injections were carried out by expulsion from a reservoir by a piston, activated on command from the vehicle control room. For the shallow releases a small volume (~500 ml) steel cylinder was used. For the 3627-m experiment about 9 liters of liquid CO2 was contained in a commercial accumulator (Parkers Airsea 7800) installed horizontally in the tool sled frame. The accumulator was connected to a set of valves and fittings, which permitted loading of the cylinder with liquid CO2 from standard gas cylinders before the dive. Procedurally, after the first filling, an accumulator gauge pressure of about 600 pounds per square inch (psi) was observed, with the piston set at maximum accumulator capacity. The gas delivery cylinder was then warmed (to compensate for expansion cooling on CO2 transfer), and the accumulator was packed in ice to lower the temperature of the contained CO2. A second filling was carried out, and the ice was removed. The filled accumulator was vented to about 700 psi as it warmed to room temperature to prevent overpressure. The system was configured to permit open contact between seawater and the ocean side of the high pressure accumulator. When the high pressure was released, and pressure increased, the decrease in volume of the contained liquid CO2 was compensated for by active piston motion (to maintain pressure equality). Camera injection of the pressure gauge during the dive showed the expected drop in accumulator pressure as the pressure-temperature boundary for liquid CO2 was approached (in practice at a depth of about 400 m), and the differential pressure across the piston dropped effectively to zero. A system check was carried out by opening the quarter-turn CO2 release valve at several depths during deployment, thereby venting small amounts of liquid CO2.
13. Images of the overflow events are posted along with other supplementary material at www.sciencemag.org/feature/data/987360.1h and at the Monterey Bay Aquarium Research Institute (MBARI) Web site www.mbari.org/ghgases/deep/release.htm.
17. The total volume of the glass tube was ~7.22 liters (diameter, 30 X 175 cm) and the initial volume of liquid CO2 was 1.8 liters. It is possible to calculate the minimum rate of water incorporation, assuming that the rate of filling ([7.2 liters — 1.8 liters]/45 hours) was equivalent to hydrate formation, hydrate density was 1.1 kg/liter, and water accounted for 71% of the mass of the hydrate (CO2·6H2O). Rate = 1.2 liters/hour X 1.1 kg/liter X 0.71 = 0.94 kg/hour. The actual rate is somewhat faster as some CO2 is incorporated into the hydrate.
20. Supported by a grant to MBARI from the David and Lucile Packard Foundation. We thank the MBARI engineers, ROV pilots, and ship’s crews for their skilled support.
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Spectroscopic Determination of the Water Pair Potential
R. S. Fellers, C. Leflorestier, L. B. Braly, M. G. Brown, R. J. Saykally* 1

A polarizable water pair potential was determined by fitting a potential form to microwave, terahertz, and mid-infrared (D2O) spectra through a rigorous calculation of the water dimer eigenstates. It accurately reproduces most ground state vibration-rotation-tunneling spectra and yields excellent second virial coefficients. The calculated dimer structure and dipole moment are very close to those determined from microwave spectroscopy and high-level ab initio calculations. The dimer binding energy and acceptor switching and donor-acceptor interchange tunneling barriers are in excellent agreement with recent ab initio theory, as are cyclic water trimers and tetramer structures and binding energies.

Much experimental and theoretical effort has been directed toward understanding the nature of the water dimer: the archetype for aqueous hydrogen bonding. Although the dimer structure and hydrogen bond rearrangement dynamics are now fairly well characterized, the equilibrium binding energy (D) and dissociation energy (D0) remain controversial, and these are crucial for properly assessing recently proposed dimer effects in atmospheric chemistry (1). Water dimer properties are most succinctly and profoundly expressed in the intermolecular potential energy surface (IPS)—the water pair potential. This pair potential is likewise essential for modeling the condensed phases of water, because it is the principal component of the force field (three- and four-body interactions are much weaker). The water pair potential has heretofore eluded accurate determination because of technological and computational impediments. Here we describe the determination of a polarizable water pair potential by regression analysis of the rotational constants, tunneling splittings, and intermolecular vibrational frequencies precisely determined from microwave, terahertz, and infrared vibration-rotation-tunneling (VRT) spectroscopy of the water dimer (2, 3). Our previous experience with simpler IPS determinations indicates that such measurements provide an exacting measure of the relevant force field (4).

Theoretical and spectroscopic studies have shown that the six-dimensional (6D) water IPS has a complex topology. There are eight identical global minima, differing only by permutations of the four hydrogen atoms and two oxygens that do not break covalent bonds [the permutation-inversion symmetry group is D8h(M)]. Ab initio calculations (5) have revealed three low-energy paths connecting these eight degenerate minima: “acceptor switching” (equivalent to a 180° rotation of the hydrogen bond acceptor about its symmetry axis), “interchange” (exchange of the role of donor and acceptor of the hydrogen bond), and “bifurcation” (exchange of bound and free hydrogens.
The equilibrium and zero-point dissociation energies are from the thermal conductivity experiments of Curtiss et al. The observables in the nonlinear least-squares regression analysis are the spectroscopically determined tunneling levels of (D₂O)₂ in the lowest two rotational states (J = 0 and J = 1) of the ground vibrational state and in J = 0 of the excited intermolecular vibrational states near 68, 83 (§), and 104 cm⁻¹. Only (D₂O)₂ data are used, because the corresponding (H₂O)₂ spectra have many more unobservable VRT states due to unfavorable nuclear spin statistics, making it difficult to determine the bifurcation or interchange splittings. In contrast, these splittings are completely determined for (D₂O)₂. Moreover, recent infrared cavity ringdown experiments by Paul et al. (9) have determined the (D₂O)₂ ground state acceptor tunneling splitting, whereas this has not been possible to do for (H₂O)₂. However, by scaling the fitted potential for (D₂O)₂ mass effects, the corresponding properties for (H₂O)₂ can be calculated.

The computationally demanding calculation of VRT states on the 6D IPS that is required for regression analysis was made possible by use of the recently developed Split Wigner Pseudo Spectral (SWPS) algorithm (10, 11), which accurately and efficiently yields the eigenstates within a scattering theory formalism. Only a subset of the available data was used in the fit, in order to make this very large calculation feasible (13 microwave transitions and tunneling splittings of the J = 0 and J = 1 ground state and 8 J = 0 terahertz transitions in the three observed vibrational bands).

With judicious selection of these data, we could avoid calculating half of the A/B states and all of the E states (Fig. 1). The latter is crucial because the doubly degenerate E states require twice as many basis functions and three times the computer processing time for convergence. This truncation does not generally affect the results of the fit, because the spectroscopic data are so highly redundant (that is, not independent), but it did preclude a direct fit of the small (~3 × 10⁻⁴ cm⁻¹) bifurcation shifts. The basis set for these calculations employed the minimum set of functions that converged the J = 0 inter-

![Figure 1](image.png)  
**Fig. 1.** The effect of the three tunneling motions on the lowest energy water dimer rovibrational state with labeled splittings. The symmetry labeling scheme is determined from permutation inversion group theory (2). These labels describe the symmetry of the different water dimer tunneling wave functions. The splitting or shift of the VRT states is inversely related to the tunneling barriers. Acceptor switching, which has the smallest barrier, causes each rovibrational state to be split into two: A₁ and B₁ (splitting denoted by a). Interchange tunneling further splits each of those states into three (splitting denoted by b and c). Bifurcation tunneling, which has the highest barrier, causes a small shift of the E²⁺ states but does not cause further splitting, because the first two motions have already resolved all the available states.

![Figure 2](image.png)  
**Fig. 2.** The water dimer. R_R, center-of-mass separation between the two monomers; θ_d, angle made by the acceptor monomer symmetry axis with R_R; θ_a, angle made by the donor monomer symmetry axis with R_R.

### Table 1. A comparison of the ground state properties of (D₂O)₂ and tunneling barriers of the IPS.

<table>
<thead>
<tr>
<th>Ground state water dimer properties</th>
<th>Experimental(D)</th>
<th>VRT (ASP-W)eo</th>
<th>VRT (ASP-W)eq</th>
<th>Ab initio(D)</th>
<th>ASP-W(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₃ (kcal/mol)</td>
<td>5.40 (0.5)</td>
<td>--</td>
<td>4.91</td>
<td>5.05</td>
<td>4.69</td>
</tr>
<tr>
<td>D₂O (kcal/mol)</td>
<td>3.66 (0.5)</td>
<td>3.46</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>R_CO (Å)</td>
<td>2.976 (0.00-0.03)</td>
<td>2.94 (3)</td>
<td>2.924</td>
<td>2.953</td>
<td>2.972</td>
</tr>
<tr>
<td>θ_y (deg)</td>
<td>57 (10)</td>
<td>41 (2)</td>
<td>48.5</td>
<td>56.0</td>
<td>64.6</td>
</tr>
<tr>
<td>θ_y (deg)</td>
<td>51 (10)</td>
<td>58 (2)</td>
<td>50.2</td>
<td>59.1</td>
<td>44.5</td>
</tr>
<tr>
<td>A (GHz)</td>
<td>124.9</td>
<td>123.7</td>
<td>115.6</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>B (GHz)</td>
<td>5.433</td>
<td>5.423</td>
<td>5.570</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>C (GHz)</td>
<td>33.11</td>
<td>30.79</td>
<td>14.94</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>μ_d (Debye)</td>
<td>2.60</td>
<td>2.65 (10)</td>
<td>2.69 (10)</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

- The B and C rotational constants and dipole moment were measured by microwave and Stark experiments of Odutola and Dyke (27). Using these data in conjunction with measurements for other dimer isotopes, they derived the equilibrium structure parameters R_CO, θ_y, and θ_y using a constrained model (rigid monomers). The structure parameters are defined in Fig. 2. The A rotation constant is estimated from the far-infrared measurements of Karyakin et al. (28).
- The equilibrium and zero-point dissociation energies are from the thermal conductivity experiments of Curtiss et al. (13).
- The VRT (ASP-W) vibrationally averaged structure was determined by the DQMC method. The rotational constants and dipole moment were measured by microwave and Stark experiments of Odutola and Dyke (27).
- The high level ab initio calculations of Mas and Szalewicz using symmetry-adapted perturbation theory (16).
- The original ASP-W potential of Millot and Stone (6) is used in the present work. The principal tunneling barriers of the VRT (ASP-W) and ASP-W surfaces are corrected to ab initio results of |Smith et al. (5) and |Wales (23). The VRT (ASP-W) and ASP-W barriers were found with the Orient program (29). Ab initio calculations were performed at the MP2 level with coordinate corrections to improve accuracy.
change and acceptor switching splittings to better than 0.02 cm⁻¹ in the ground state. Typically, a single iteration of the fit required 12 to 20 computing hours on an IBM RS/6000 590 workstation. The total computational effort required about 6 months of computing time.

After exploring the sensitivity of the data to the parameters in ASP-W, we concluded that changing the exchange-repulsion terms had the largest effect on the spectra, which is consistent with the findings in our previous Ar–H₂O, Ar–NH₃, and (HCl)₂ IPS determinations (4, 12). Ultimately, eight of the exchange-repulsion parameters describing this interaction were varied in the fit. The final fitted values, compared with original ASP-W parameters, are also available (7).

The quality of the fitted IPS, which we call VRT (ASP-W), was assessed in several ways. Table 1 shows the excellent agreement of the VRT (ASP-W) ground state water dimer structure (Fig. 2) and dipole moment with experimental and ab initio results, and that they are much improved relative to ASP-W. The fitted potential was also used to predict VRT states up to total angular momentum J = 2 not explicitly included in the fit, yielding excellent agreement (largest error = 0.16 cm⁻¹, or <1% of transition frequency, with most errors being an order of magnitude smaller). For the excited VRT states near 68, 83, and 104 cm⁻¹, the agreement with experimental results is not as good (~1 to 5 cm⁻¹), but it is nevertheless clear from Fig. 3 that VRT (ASP-W) reproduces the energy-level spectrum of the water dimer very well, and this is a most demanding test of a potential surface. For comparison, we have computed these VRT states on a number of other potentials (11) (including TIP4P; SPC; MCY; and polarizable SPC, RWK2, NEMO3, TIP-FQ, ASP-S, and ASP-W) and have found that all produce energy-level patterns that deviate significantly from experimental results, as shown for the original ASP-W, previously considered to be the best dimer IPS.

One of the most important properties of the water dimer is the binding energy (Dₒ). The most often quoted experimental value is 5.4 ± 0.7 kcal/mol, derived from the dissociation energy measured in thermal conductivity experiments (13). Reimers et al. (14) recommended the same value for Dₒ with tighter error bars (5.4 ± 0.2 kcal/mol). This value is too large because it is obtained with the use of crude harmonic ab initio vibrational frequencies. Ab initio calculations of Dₒ have given values ranging from 5.6 to 4.6 kcal/mol, although the most recent and sophisticated calculations converge to a value of 5.0 ± 0.1 kcal/mol (15–18). Our VRT (ASP-W) potential gives Dₒ = 4.91 kcal/mol. Using diffusion quantum Monte Carlo (DQMC) methods (19) to perform the requisite vibrational averaging, we have also calculated the (D₂O)$_₂$ dissociation energy (Dₒ) of the ground state as 3.46 kcal/mol, which compares well with experimental results (Table 1).

Second virial coefficients (SVCs)—coefficients of the squared density in the power series expansion of the equation of state P/R for a vapor—are a time-honored measure of a pair potential (20). Comparison of the temperature dependence of SVCs calculated from VRT (ASP-W) with experimental values obtained from H₂O and D₂O steam measurements (21) shown in Fig. 4 constitutes a stringent test of the overall validity of our potential, because SVCs are sensitive to both the attractive well depth and the angle-averaged potential (22). Essentially perfect agreement is found for both H₂O and D₂O iso-
Design and Self-Assembly of Open, Regular, 3D Mesosstructures

Tricia L. Breen, Joe Tien, Scott R. J. Oliver, Tanja Hadzic, George M. Whitesides*

Self-assembly provides the basis for a procedure used to organize millimeter-scale objects into regular, three-dimensional arrays (“crystals”) with open structures. The individual components are designed and fabricated of polyurethane by molding; selected faces are coated with a thin film of liquid, metallic alloy. Under mild agitation in warm, aqueous potassium bromide solution, capillary forces between the films of alloy cause self-assembly. The structures of the resulting, self-assembled arrays are determined by structural features of the component parts: the three-dimensional shape of the components, the pattern of alloy on their surfaces, and the shape of the alloy-coated surfaces. Self-assembly of appropriately designed chiral pieces generates helices.

We describe a procedure that uses self-assembly of patterned, three-dimensional (3D), mesoscale (millimeter- to centimeter-scale) objects to generate open, regular, 3D structures. These types of structures may eventually find use as the cores of densely interconnected, 3D electronic and optical elements for high-performance computation and sensors. We prepared millimeter-scale objects (both polyhedra and more complex shapes designed to form an extended lattice), coated selected faces with a film...