The Structure of Nature's Solvent: Water

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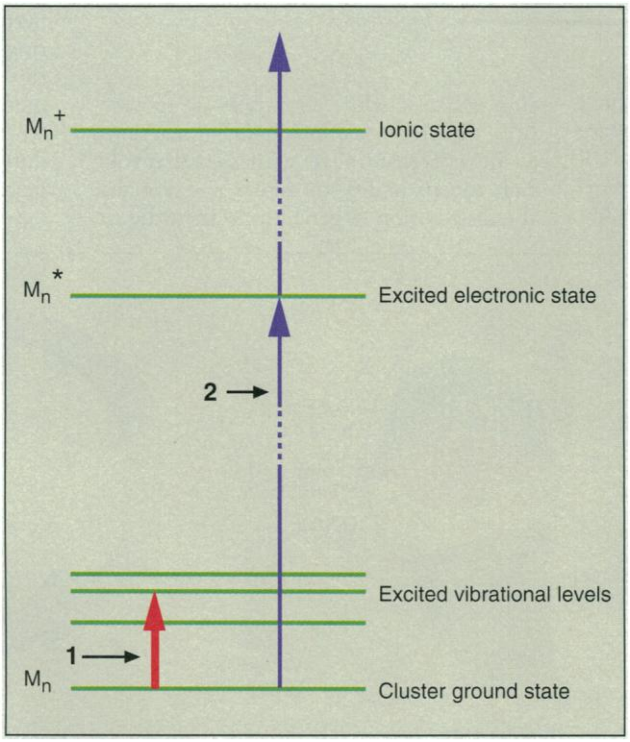
Simultaneous advances in experimental and theoretical methods are providing new insights into the intermolecular interactions that control the dissolution of chemicals in water. Progress in theoretical methods and computer technology has greatly extended the range of computational techniques for modeling molecular clusters. Although water clusters have long been the subject of theoretical studies, only recently has it become feasible to perform accurate computational studies on water clusters and molecule-water clusters with more than two water molecules (*1*). On the experimental side, clusters of water molecules, and of water molecules with another chemical species, can now be constructed one molecule at a time. The properties of these unique "aqueous solutions" can be measured spectroscopically and form a rich test bed for guiding the development of detailed molecular descriptions of solvation. As Pribble and Zwier report on page 75 of this issue (*2*), such spectroscopic methods can yield interesting information about cluster properties as the number of water molecules increases.

Molecular clusters can be formed by condensation during expansion of a high-pressure gas mixture (for instance, 98% helium, 1% water, and 1% benzene) into vacuum. Depending on the concentrations and pressure, the maximum cluster size produced can range from a few molecules to many hundreds (*3*). Such molecular clusters are often best examined with vibrational infrared (IR) spectroscopy, because it is capable of directly probing the inter- and intramolecular binding forces in the cluster. An analysis of these forces provides a direct measure of the properties of the cluster as well as indirect information about the structure of the cluster.

With the advent of intense cluster beam sources (*4*) and powerful tunable IR lasers (*5*), it has become possible to directly observe the IR absorption spectra of clusters. However, because it is difficult to assign a particular IR absorption feature to a specific cluster, this method has only been applied to molecular beam studies containing small clusters (up to three molecules). In their report, Pribble and Zwier describe a method by which the IR spectra can be correlated with a specific size cluster (*2*). Rather than measuring the absorption directly (transition 1 in the figure), the depletion caused by the absorption is determined by the reduction in the number of ions produced by the two-step process 2. In process 2, the cluster (M_n) absorbs an ultraviolet (UV) photon and is excited to a molecular electronic excited state. This is followed by a second photon, which leads to cluster ionization. If this resonant two-photon ionization process does not result in fragmentation of the cluster, then mass spectroscopy can be used to determine the size of the cluster. The experiment is actually performed by selecting a UV laser wavelength for the ionization of the cluster of interest and then scanning the wavelength of an IR laser focused on the same portion of the molecular beam. When the cluster absorbs from both lasers, there is a reduction in the signal associated with process 2. Hence, recording the ion signal as a function of the IR laser frequency generates the IR spectrum of the cluster. Although the feasibility of this approach was demonstrated some years ago (*6*), it has only become practical with the recent development of intense, tunable IR lasers (*5*).



The detection of IR absorption (transition 1) by clusters (M_n) through reduction of the resonant two-photon ionization rate (process 2) caused by ground-state depletion. High sensitivity and cluster size identification are achieved by detecting the ions (M_n^+) in a mass spectrometer.

Pribble and Zwier draw three important inferences from their study of the vibrational spectra of benzene-water clusters in the OH stretch region (3000 to 4000 cm^{-1}). First, they note that the OH stretch frequencies in benzene-water clusters are similar to those observed or computed for the corresponding water clusters. The water cluster appears to be little perturbed by the presence of the benzene molecule. This led the authors to conclude that, even in these small clusters, "the benzene and water molecules...can be thought of as 'immiscible'." That is, the benzene molecule is attached to the surface of a water cluster rather than being immersed within it.

For C_6H_6-$(H_2O)_n$ (i = 3 to 5) clusters, they found that the OH stretches could be divided into three types, corresponding to "free," "single donor," and "π H-bonded" OH groups [see figure 2 of Pribble and Zwier (*2*)], and concluded that benzene is attached to the edge of the $(H_2O)_n$ (i = 3 to 5) cluster by a bond between the π system of benzene and one of the "free" OH bonds in the water cluster. This conclusion is supported by the correlation between the frequency shifts predicted from ab initio studies of the pure water clusters and the observed frequency shifts in the corresponding benzene-water clusters: n of the OH stretching frequencies can be attributed to the "single donor" OH groups in the pure water cluster, $n - 1$ can be attributed to the "free" OH groups, and the last OH stretch frequency, which ranges from 3657 cm^{-1} in C_6H_6-$(H_2O)_3$ to 3646 cm^{-1} in C_6H_6-$(H_2O)_5$, can be attributed to the "π H-bonded" OH group.

Finally, the spectra of the C_6H_6-$(H_2O)_n$ (i = 6 to 7) clusters show a number of features quite unlike those found in the smaller clusters. By comparing the measured transitions with ab initio calculations on the corresponding pure water clusters, the authors speculate that these features are associated with the formation of water clus-

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ters that contain water molecules that act as "double donors" [see figure 2 of Pribble and Zwier (*2*)]. This is consistent with theoretical calculations for the larger water clusters, which predict that the lowest energy structures are no longer the ring structures formed entirely from single-donor water molecules [again, see figure 2 in (*2*)], but also include double-donor waters.

Understanding the fundamental interactions between a molecule and water is the cornerstone of our understanding of aqueous solutions. The observations and conclusions drawn by Pribble and Zwier (*2*), if they prove to be correct, add new insights into our understanding of the forces between benzene and water, a classic example of a hydrophobic interaction. This work also illustrates the synergism that has developed between experimental and theoretical studies in modern chemical physics. The information from each is in some measure incomplete; but combined, they can provide definitive answers to long-standing chemical questions. The experimental studies of Pribble and Zwier will likely stimulate theoretical studies of benzene-water clusters to provide further validation of and insight into the conclusions drawn by these authors.

References

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Genes on the Wing

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Discovering the mechanisms by which structure emerges from an initially homogeneous field of cells continues to be one of the fundamental problems in developmental biology. There are many such mechanisms—generally collected under the term "pattern formation." Among the problems in the pattern formation field are such disparate questions as: What determines the location where gastrulation will begin in a spherical embryo, the points where limb buds will develop along the flank of an embryo, the pattern of five bones in an initially featureless paddle-shaped hand primordium, the division of a cylindrical embryo into segments, or the placement of an eyespot on the blank, uniform epithelium of a butterfly wing? Occasionally structure is organized around irregularities that are set up by external events such as fertilization, gravity, or graded distributions of chemicals that the mother incorporates into an egg cell, but in many cases such singularities or prepatterns are unknown. The mechanisms of pattern formation are generally believed to require interactions among molecules that specify the fates of cells. Some of these molecules are the direct products of genes, others alter the expression of genes, while yet others are metabolites, the products of biochemical reactions.

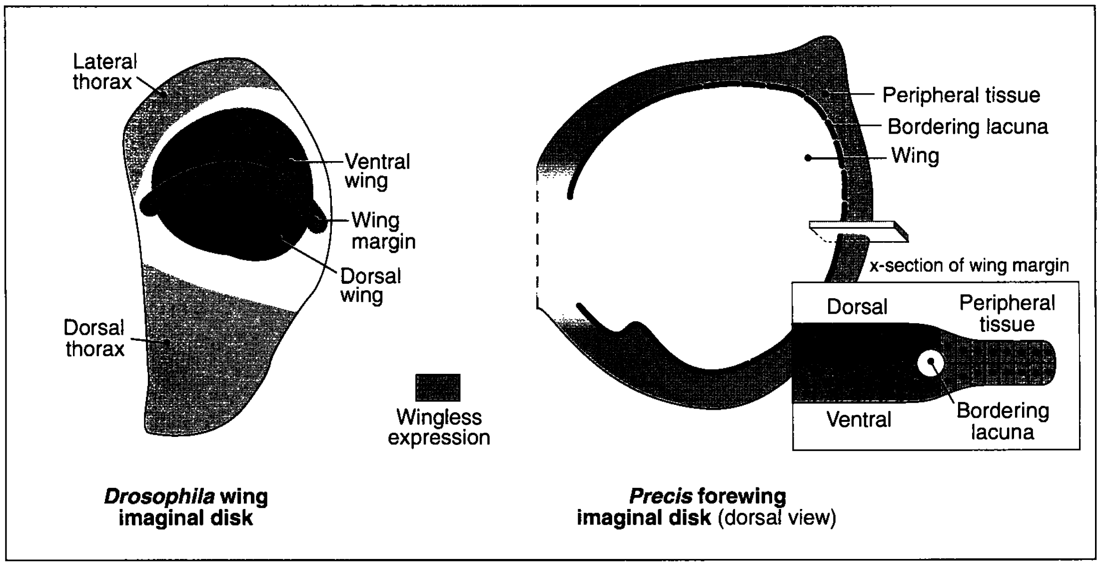

Fig. 1. Wing development in fruit flies and butterflies. In insects with complete metamorphosis, all adult appendages develop during larval life as internal imaginal disks. Imaginal disks of the higher Diptera, like *Drosophila*, are complex structures that undergo substantial morphogenesis in their metamorphosis to the adult forms. The wing imaginal disk, for instance, contains tissues that will make a large portion of the thorax, and the wing portion is folded open, so that the distal wing margin is represented by a line that runs in an arc across the center of the disk. The wing imaginal disk of butterflies is much simpler, consisting of two flat monolayers of cells, appressed to each other, which will form the dorsal and ventral surfaces of the wing. In butterflies, only the central portion of this epithelial sheet will form the adult wing, while the peripheral tissue undergoes programmed cell death during metamorphosis.

Recent years have witnessed a revolution in our ability to detect and visualize the distribution of gene products in the tissues of developing organisms. With these new eyes, we can see molecular markers of early developmental events that were previously invisible and inaccessible. Much of this work has focused on the early embryonic development of the fruit fly, *Drosophila melanogaster*, in which we now know more about the early molecular events of development than in any other species of plant or animal. For instance, we know that segmentation in the *Drosophila* embryo is preceded by a complex and dynamic pattern of gene expression, in which half a dozen or more genes become expressed in bands and rings whose positions indirectly define those of the future body segments (*1*). Segment specification is followed by an almost equally complex pattern of gene expression, different in each segment, that presages the development of the characteristic morphology of each segment. In the imaginal disks of *Drosophila* embryos and larvae, there are likewise patterns of gene expression that correspond to the future wing margin, appendage tips, and to dorsal, ventral, anterior, and posterior compartments (*1*, *2*).

This treasure trove of molecular markers for early developmental events could only have been developed in a species such as

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