The Spectroscopy of Molecular Clusters

Much of our knowledge about the strong chemical forces that hold molecules together has been obtained through spectroscopy, the study of how light is absorbed and radiated by matter. Recently, there has been rapid progress in the use of high-resolution spectroscopy to study small clusters of molecules, enabling researchers to probe the weak forces between molecules in unprecedented detail.

Although weak, these intermolecular forces control a vast range of phenomena, including the properties of gases, molecules in solution, and proteins and enzymes in biological systems. While molecules in a dilute gas largely interact as isolated pairs that collide with each other, the more densely packed molecules in a liquid or solid state depend on the simultaneous interactions between many neighbors. One only needs to compare driving on an interstate in Nebraska with the freeways of Los Angeles to understand the added complexities which arise as the density of cars or molecules increases. To address these issues, scientists are now scrutinizing small aggregates of molecules, called clusters, that provide a testing ground between the two extremes where the complexities in dense bulk materials can be systematically approached by increasing the size of the cluster one molecule at a time.

An example of a simple cluster is the water "dimer," consisting of a pair of H₂O molecules bonded together. The interactions between the two molecules in the dimer serve as an excellent illustration of the issues at hand. Due to the nature of bonding in water, the forces between the two molecules depend not only upon the distance between them, but also their relative orientation. The result is a potential energy "surface," which has a deep well corresponding to the equilibrium "hydrogen bonded" structure of the water dimer, in which a hydrogen atom associated with one molecule is bound to the oxygen atom of the other. In analogy with a ball rolling to the bottom of the hill, the tendency is for the dimer to fall into this deep well, where its configuration is reasonably well defined. Spectroscopy at microwave frequencies has been extremely effective at characterizing the bottoms of these wells for a large number of systems. However, to fully understand the interactions between the molecules we must develop methods for getting the dimer out of the well, and exploring the entire range of orientations and separations. This is much like taking the ball that is sitting in the valley and throwing it up into the hills.

Recent developments in high-resolution infrared spectroscopy have provided the tools needed for "throwing" the dimer far from its equilibrium geometry, allowing researchers to manipulate the relative motions of two molecules in a cluster. The infrared laser light can initiate vibrational motion between the molecules in a very controlled fashion. In many cases, the infrared light has sufficient energy to rupture the weak bond or bonds of a cluster, affording researchers the opportunity to trace the energy from the point at which it is deposited to the point at which the bond is broken. For example, studies have been performed on how infrared light breaks up a cluster consisting of two H₂F molecules. Recent experiments on this H₂F dimer have provided a detailed picture of how the two "hot" HF product molecules push off and gyrate away from each other, and how such molecular gymnastics depends on the way in which the cluster is initially excited into a higher-energy state. The job of the scientist is then similar to that of the sheriff who, upon arrival on the scene of an accident, tries to recreate the events that led to the wrecked cars. This approach, when aided by theoretical calculations, allows us to predict the configurations of the clusters, has provided us with new insights into the processes that lead to the rupture of the bond.
In progressively building up our clusters to the size of macroscopic particles, we must address one very important question: once we know in detail the forces between a pair of, say, H$_2$O molecules, do we really know how to describe the much more complex forces in a droplet or an ice crystal? To extend a previous metaphor, how must we modify the basic driving skills learned on the Nebraska interstate to survive on the Los Angeles freeways, where a sudden lane change of one car can cause two others to collide? The key lies in the forces that arise from the collective influence of more than two molecules at a time. In studying these “non-pairwise additive forces,” exciting progress has recently been made in spectroscopic studies of three-molecule clusters, such as (H$_2$O)$_3$, (HCN)$_3$, and (HF)$_3$, which form structures of repeating rings. This sequential approach, which allows us to systematically increase the size and complexity of the cluster under investigation, is exemplified in the (Ar)$_n$—HF(n+1–4) and (Ar)$_n$—HCl(n+1,2) series. Given that the dimer studies enable us to determine the two-body forces in considerable detail, these larger clusters are beginning to provide similar detail on the more subtle but enormously important many-body forces that play a key role in the properties of solids and liquids.

Roger E. Miller  
University of North Carolina  
(919-966-5433)

David J. Nesbitt  
University of Colorado  
(303-492-8857)