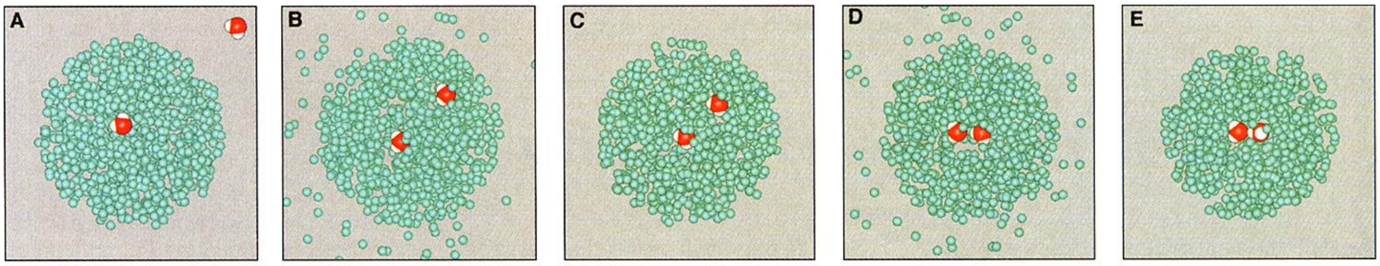
PERSPECTIVES: MOLECULAR SPECTROSCOPY

Nanomatrices Are Cool

Giacinto Scoles and Kevin K. Lehmann

Supersonic free jets and matrix isolation are the two most commonly adopted methods for probing isolated molecules at low temperatures. Several new techniques are currently being developed to overcome some of their limitations. Three recent papers by Nauta and Miller (*1–3*) and a report by Weber *et al.* on page 2461 of this issue (*4*) illustrate the power of one of these techniques, nanomatrix isolation spectroscopy (*5*), in which inert gas clusters or droplets are used to isolate and characterize molecules and complexes not accessible by other techniques. The results shed light on important issues such as ion solvation and structural metastability.

In helium nanodroplet isolation (HENDI) spectroscopy (*6*, *7*), a beam of tiny ^{4}He droplets of 1000 to 100,000 atoms is passed through a low-pressure vapor of the substance to be examined (*8*). After picking up one or more dopant molecules, the droplets return rapidly to their "equilibrium" temperature of 0.38 K (*9*) (see panel B in the figure) and carry the dopants into the next chamber, where they are interrogated spectroscopically. In a comment to (*9*), 2 years ago, we argued that, because of their low temperature and lack of strong perturbations, superfluid helium nanodroplets may well be considered the ultimate matrix-isolation medium (*5*).



Assembling clusters in cold nanodroplets. A water molecule approaches a liquid helium nanodroplet that contains another molecule (**A**). Upon impact and solvation, energy is released by evaporation (**B**). The two molecules are pulled together inside the droplet by long-range forces (**C**). The energy liberated in forming the bimolecular complex is released again by evaporation (**D**). The cold complex is now ready for spectroscopic interrogation (**E**).

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Has the new method kept its promises? In our view, the answer is an unqualified yes. The papers by Nauta and Miller (*1–3*) and Weber *et al.* (*4*) demonstrate the fast progress in this area. Nauta and Miller work with helium nanodroplets, whereas Weber *et al.* use much smaller nanomatrices of argon (just a few atoms), but the papers share the idea of interrogating a cold molecule by "matrix spectroscopy in the gas phase" (*10*). Weber *et al.*'s discovery that similarly to the case of helium, the perturbations induced by argon nanomatrices on negative ions are weak, brings with it the possibility of mass selection, a clear advantage for the study of complex multicomponent mixtures.

Previous work with HENDI has demonstrated the selective production of the metastable high spin states of alkali dimers and trimers (*11*). Nauta and Miller's work demonstrates the wider applicability of the method for the preparation of metastable molecular complexes in liquid helium nanodroplets, with much higher selectivity than other matrix isolation methods. For polymers of strongly dipolar molecules, HCN (*1*) and HCCCN (*2*), only the hydrogen-bonded linear chains are observed in HENDI spectroscopy, despite the fact that for the longer chains, cyclic or antiparallel chains are lower in energy. Only the latter are observed in a supersonic jet. This self-assembly of a unique, higher energy form is due to permanent dipole-dipole interactions that dominate at long range, steering the molecules toward a short-range local energy minimum. The rapid cooling provided by the liquid environment is likely to be critical in preventing the energy released upon hydrogen bond formation (see panel D in the figure) from annealing the polymer to its global minimum. The size of the linear chain that can be assembled turns out to be precisely limited by the droplet diameter.

More recent work by Nauta and Miller (*3*) deals with water clusters formed by the same technique. Clusters up to the hexamer were previously studied by Saykally and co-workers using a supersonic expansion in a slit jet (*12*), but only the lowest energy isomer of each cluster could be probed. As in a previous HENDI study of the trimer (*13*), Nauta and Miller find that the OH stretching vibrational spectra of water clusters containing two to five molecules observed by HENDI spectroscopy are the same (except for improved resolution due to lower temperature) as those produced by jet expansion. In contrast, the hexamer has a very different spectrum. In the jet expansions, the hexamer forms a cage structure believed to be the global minimum structure, whereas the HENDI spectrum for the hexamer is consistent with a cyclic, chiral, hydrogen-bonded structure that is the same as the basic hexagonal subunit in common ice. This structure has also been predicted to be present as transient structural motif in liquid water. Thus, the ability to observe this particular isomer of the water hexamer helps bridge the microscopic and the bulk properties of water.

Why is the cyclic metastable structure selectively formed in the nanodroplets? Contrary to the case of HCN, the water dimer structure is nonlinear, and the formation of the cyclic trimer requires only a small distortion of the hydrogen bonds. The other cyclic clusters form by sequential insertion of water molecules in an environment where energy dissipation is fast and facile. Out-of-plane isomerizations are presumed not to occur thermally because of large barriers and cannot be tunneled into because of the need for large changes in the heavy atom positions. This suggests that formation of metastable isomers should be the rule for HENDI self-assembly. We and our co-workers have found that the dimers of $(CH_3)_3SiCCH$ formed in He nanodroplets are also linear symmetric tops, despite the fact that a slipped antiparallel structure is likely to be the lowest energy isomer.

Water is also the main protagonist of the report of Weber *et al.* (*4*), who demonstrate that argon nanomatrix isolation spectroscopy can be used to characterize the solvent structure in a complete hydration shell around an anion, in this case O_2^-. The presence of the Ar atoms, which are easily evaporated, provides a convenient way to help dissipate the sizable solvation energy

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released when the anion is hydrated. Without such cooling, the hydrated species are fluxional, likely sampling several isomeric structures, which results in diffuse infrared spectra carrying limited structural information. For complexes with an incomplete hydration shell, the spectra remain diffuse even when the complexes are cooled by Ar evaporation. In contrast, the OH stretching fundamental spectrum for the tetrahydrated O_2^- shows well-defined structure, in excellent agreement with that predicted for a highly symmetric hydrogen-bonded structure. As in the Nauta and Miller work, the OH stretch spectrum is particularly sensitive to the structural properties of the complex because of its strong dependence on the degree and cooperativity of hydrogen bonding.

If one neglects the possible difficulties of assembling superoxide tetrahydrate in liquid helium nanodroplets, the use of Ar is, in principle, less favorable than that of He because of the larger perturbations and the warmer temperatures present in Ar nanomatrices. Nevertheless, the observed line widths for the tetrahydrate were sufficiently narrow compared with those of the less hydrated complexes to enable reliable structural assignment. With improved spectral resolution, one can foresee observation of rotational or rotational-tunneling structure, which would allow a more detailed comparison of experiment with theory for these important molecular species that are the cornerstones of macroscopic aqueous solvation.

Little is known about the size and nature of chemical reaction barriers smaller than ~0.1 kcal/mol (*14*). HENDI spectroscopy may be useful here, as the low-temperature environment is expected to suppress almost all reactions with an appreciable barrier, leading instead to the formation of van der Waals complexes, the presence of which would be indicative of even a small barrier. The structural selectivity demonstrated above, may allow the detection of the angular dependence of reaction barriers by allowing for the control of the matrix orientation in bimolecular encounters, much as it is done in the gas phase (*15*). HENDI may also be used to study isomers of complex organic molecules. Lindinger *et al.* have shown (*16*) that the number of tyrosine and tryptophan isomers detected by HENDI is smaller than that detected in the warmer but still cold environment of a supersonic free jet (*17*). Photon-induced annealing of the isomers of these and other, larger, molecules should teach us a great deal about the intramolecular dynamics, and possibly the folding, of complex molecules.

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18. We thank our students and co-workers for useful discussions and their contributions. In particular, we are indebted to C. Callegari, who drafted the figure.

PERSPECTIVES: ASTRONOMY

Stars at the Edge of Stability

Norbert Langer

The most massive stars known today can, for short periods of time, erupt, shedding amounts of mass and energy comparable to a supernova. Such an eruption does not end a massive star's life but is key to its ultimate fate. For example, Eta Carinae, today invisible to the naked eye, erupted in the 19th century, making it the second brightest star in the sky for more than 10 years (*1*). The ejected matter now forms the strongly bipolar Homunculus nebula (see the left panel in the figure) (*2*). About a dozen such luminous blue variables (LBVs) are known today (*3*). Their radius and surface temperature can remain variable on time scales of months or more, for decades to centuries after the eruption. Intense recent research activity, fueled not least by the Hubble Space Telescope, has shed some light on the eruption mechanism, with possible clues for the formation of massive stellar black holes and gamma ray bursts (GRBs), for which massive stars are thought to be progenitors (*4*).

There is one main factor that destabilizes LBVs: their huge luminosity. Stars shine brighter the more massive they are. This trend is so steep that the most massive stars—comprising about 100 solar masses ($M_\odot$) but a millionfold brighter than the sun—extinct their fuel in less than a per mil of the sun's lifetime. The enormous luminosity is produced in the star's deep interior, and the huge number of photons carrying it exert a strong outward force while traveling to the surface. This causes two instabilities. First, the stellar interior becomes convectively unstable, leading to a millionfold acceleration in the transport of energy to the surface and relieving the star from an otherwise unbearable pressure. Second, the photons escaping from the star push on the ions in the star's atmosphere so vigorously that they drive a very dense and powerful outflow, which can reduce the star's mass substantially during its short lifetime and creates huge bubbles in the interstellar medium.

Both instabilities—convection and radiation-driven winds—already occur in stars more massive than 10 $M_\odot$ but do not lead to their destabilization. However, the most massive stars are 100 times more luminous than 10 $M_\odot$ stars. In the outer parts of such stars, the hydrostatic equilibrium may break down as the radiation pressure gradient overwhelms gravity: The star exceeds its Eddington limit, the upper luminosity limit that can be radiated by an object of a specified mass. This is thought to lead to the eruptions seen in LBVs (*5*).

The morphology of the eruption debris lends strong support to the Eddington mechanism. Recent imaging and spectroscopic studies found that all but one nebula around LBVs show a bipolar geometry (*6*). Whatever causes LBV eruptions is thus not spherical but axially symmetric. Axial symmetry is expected when a rotating star exceeds its Eddington limit, as the centrifugal force breaks the spherical symmetry otherwise maintained by the balance between gravity and radiation. This has been demonstrated by models for the formation of the Homunculus nebula (*7*).

On the other hand, the axial symmetry of the eruption debris may also be caused by a close binary companion. Such a companion could exert a force on the surface of the LBV and thereby trigger an eruption, or it could shape the debris through its gravitational field, its radiation, or its stellar wind. In the latter case, the symmetry axis of the debris would not go through the LBV but through the center of mass of the binary

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