Struct. **26**, 567 (1997); D. T. Chiu and R. N. Zare, *Chem. Eur. J.* **3**, 335 (1997).

10. A. Moscho, O. Orwar, D. T. Chiu, B. P. Modi, R. N. Zare, *Proc. Natl. Acad. Sci. U.S.A.* **93**, 11443 (1996). The reagent molecules of interest are introduced into the vesicles during the formation process. A main advantage of this preparative technique is speed; unilamellar vesicles can be prepared within 2 min. This advantage is particularly important for encapsulating and reacting labile molecules for which long preparation times might lead to degradation. Another important advantage is the flexibility of the technique: the internal and external buffer solution, reaction chamber size, and reaction chamber surface properties can be easily varied to mimic the particular cell types or organelles of interest.
11. D. T. Chiu *et al.*, *Anal. Chem.* **69**, 1801 (1997).
12. Chernomordik *et al.*, *Biochim. Biophys. Acta* **902**, 360 (1987).
13. C. Wilhelm, M. Winterhalter, U. Zimmermann, R. Benz, *Biophys. J.* **64**, 121 (1993).
14. D. C. Chang and T. S. Reese, *ibid.* **58**, 1 (1990).
15. U. Zimmermann, *Biochim. Biophys. Acta* **694**, 227 (1982); N. G. Stoicheva and S. W. Hui, *ibid.* **1195**, 31 (1994); S. W. Hui and D. A Stenger, *Methods Enzymol.* **220**, 212 (1993).
16. N. Düzgünes and J. Wilschut, *Methods Enzymol.* **220**, 3 (1993).
17. The electrically induced poration or fusion of cells is used extensively in biological research for introduction of molecules or genes into cells or for creation of new cell lines (*15*). These experiments typically are performed in a chamber, in a random manner, where several million cells are electroporated or fused simultaneously, with a relatively low yield. In our experiments, we extend the use of this physical principle to the level of single vesicles with subcellular dimensions. This extension is made possible by the use of a highly localized electric field from a pair of ultramicroelectrodes, precise manipulation techniques, and sensitive laser-induced fluorescence detection.
18. D. A. Stenger and S. W. Hui, *Biophys. J.* **53**, 833 (1988); D. Needham, *Methods Enzymol.* **220**, 111 (1993).
19. Electroporation and electrofusion of vesicles are relatively straightforward to perform. The procedure of selecting, isolating, and aligning two vesicles of different contents before fusion, however, requires some skill and experience. This procedure might be simplified by using micromachined channels and wells as conduits for selection and isolation of vesicles.
20. R. Y. Tsien, *Annu. Rev. Neurosci.* **12**, 227 (1989).

21. Supported by New Energy and Industrial Technology Development Organization of Japan under the International Joint Research Program, the U.S. National Institute on Drug Abuse (DA09873), the Swedish Foundation for Strategic Research (SSF), and the Swedish Natural Science Research Council (NFR) (10481-305-308 and -309). We thank S. Orwar for technical assistance with image processing. C.F.W. acknowledges support from the Stanford Graduate Fellowship. A.G. and B.P.M. are Stanford University Bing Chemistry Summer Undergraduate Research Fellows. B.P.M. acknowledges funding by a Howard Hughes Summer Fellowship from the Stanford University Department of Biological Sciences.

13 April 1998; accepted 16 February 1999

Nonequilibrium Self-Assembly of Long Chains of Polar Molecules in Superfluid Helium

K. Nauta and R. E. Miller*

It is shown that in the low-temperature (0.37 kelvin) environment of superfluid helium droplets, long-range dipole-dipole forces acting between two polar molecules can result in the self-assembly of noncovalently bonded linear chains. At this temperature the effective range of these forces is on the nanometer scale, making them important in the growth of nanoscale structures. In particular, the self-assembly of exclusively linear hydrogen cyanide chains is observed, even when the folded structures are energetically favored. This suggests a design strategy for the growth of new nanoscale oligomers composed of monomers with defined dipole (or higher order) moment directions.

It is well known that as two point dipoles approach from long range they prefer to orient in a head-to-tail configuration (*1*). An analogous and perhaps more familiar case is that of two approaching magnets that orient such that their north poles point in the same direction. These simple ideas would lead one to predict that highly polar monomer units might assemble head-to-tail to form linear polymer chains. However, at room temperature the average rotational energy is large relative to the dipole-dipole interactions, such that the $1/R^3$ interaction (R being the distance between the dipoles) motionally averages (integrated over all angles) to $1/R^6$ (*2*), greatly reducing its range. As a result, dipole-dipole forces generally play only a minor role in determining the local "structure" of simple liquids (*2*). Chainlike structures are seen in some polar solids, such as crystalline HCN (*3*). However, the lateral dispersion interactions between chains (the crystal force field) are important in stabilizing such structures, and it is not obvious that they will be stable in the gas phase, where more compact structures better optimize the weak interactions between the molecules. We might therefore expect that the strong dipole-dipole interactions will dominate only for short chains and that the energy penalty for keeping the system linear will increase with chain length to the point where the system eventually folds. Ab initio calculations have been performed for isolated HCN complexes that confirm this general trend (*4–6*).

In this study we show that polar monomers can self-assemble exclusively into extended linear chains in superfluid liquid helium droplets. These droplets represent a spectroscopic matrix (*7*) with many interesting properties, including a low-temperature (0.37 K) (*8*) and a weakly interacting and homogeneous environment that results in small vibrational frequency shifts and high spectral resolution (sufficient to show rotational structure) for solvated molecules (*8–11*). Hydrogen cyanide was chosen for this study because of its large dipole moment (3 D) and the existence of previous gas-phase studies of its complexes (*12–15*).

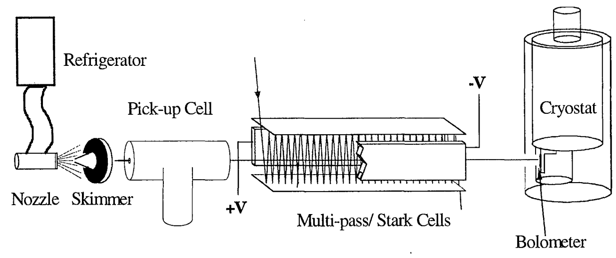
In our experimental apparatus (Fig. 1), the helium droplet source consists of a 5-μm-diameter nozzle operated at about 20 K, through which ultrapure helium is expanded from a pressure of 50 bar. Under these conditions helium droplets with a mean diameter of about 7 nm (4000 atoms) are formed. These droplets then pass through a pick-up cell maintained at an HCN pressure between 10^{-6} and 10^{-5} mbar. In this region, HCN molecules are captured individually by the helium droplets and cooled to 0.37 K (*8*, *10*). The seeded droplets then pass through the laser excitation region and are detected by either the bolometer (*16*) or mass spectrometer. Vibrational excitation and relaxation of the molecules in the helium droplet result in the evaporation of several hundred helium atoms, reducing the total flux to the detectors. The electrodes shown in Fig. 1 were used to apply a large electric field to the laser excitation region. The resulting pendular-state spectroscopy (*17*) was an essential part of assigning the spectra of the polar chains.

In a gas-phase free jet expansion the most stable isomer of a complex tends to form, and therefore the experimentally determined geometry is often the same as the ab initio global minimum structure. Only when there are a number of isomers with similar energies does one expect to observe the formation of more than one of them (*18*, *19*). This can be explained by noting that the clusters are formed in the high-density, relatively hot region of the expansion where there is still sufficient energy to surmount any barriers on the potential energy surface to reach the global minimum. Subsequent two-body collisions with the carrier gas then cool the complex to the very low temperatures typical of free jet expansions ($\sim$1 K), thereby trapping the system in the global minimum. The HCN trimer

Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599, USA.

*To whom correspondence should be addressed. E-mail: remiller@unc.edu

Fig. 1. Schematic diagram of the experimental apparatus. All spectra reported in this paper were recorded with the bolometer as the detector. The laser is a tunable, infrared F-center laser.



forms both linear and cyclic isomers in a free jet expansion (*14*, *15*), suggesting that they have comparable energy, and this has been confirmed by ab initio calculations (*5*). Presumably the strain that exists in the cyclic trimer is compensated for by the additional hydrogen bond and the (lateral) interactions gained from having the more compact structure. Larger gas-phase HCN clusters formed by free jet expansion have all been shown to be nonpolar (*20*), suggesting the formation of some kind of folded (cyclic or antiparallel) structures. Once again, this is in agreement with calculations (*4–6*).

We began the spectral search in the helium droplet experiments by scanning the laser through the region corresponding to the non–hydrogen-bonded C-H stretch. The first bands observed were those associated with the linear dimer (3308.06 cm^{-1}) and trimer (3306.60 cm^{-1}), shifted only slightly from their gas-phase positions [3308.3175 cm^{-1} and 3306.8025 cm^{-1}, respectively (*13*, *15*)]. In the absence of an electric field, both of these bands are rotationally resolved in the helium droplets, enabling a definitive assignment. It is interesting to note, however, that the cyclic trimer band is completely absent in the helium droplet spectrum. For the larger clusters of interest here, the spectra are not rotationally resolved, and we must use other methods to make the appropriate assignments.

A scan to the red of the C-H stretch of the monomer (which has its vibrational origin in helium at 3311.20 cm^{-1}) was recorded in a dc electric field of 30 kV/cm (Fig. 2). This large electric field effectively collapses the rotational band contours by orienting the dipoles (*17*), providing the spectral resolution needed to separate the features associated with the larger clusters. The signals in this spectrum are also considerably enhanced compared with those obtained at zero field, as a result of the compression of the entire spectrum into a single peak and the orientation of the transition moment along the laser polarization direction (parallel to the dc field), which optimizes the excitation efficiency. The frequency shifts relative to the monomer are small for all of these bands, indicating that they are associated with free C-H stretch vibrations. The very regular progression suggests the assignments given in the figure, namely with increasing red shift from the monomer, to the linear dimer, trimer, tetramer, pentamer, hexamer, and heptamer. This assignment of the size is confirmed by recording the signals as a function of the pick-up cell pressure (*21*, *22*), the larger cluster peaks requiring higher pressures.

A plot of the frequency shift as a function of cluster size (Fig. 3A) shows that these shifts begin to converge for large clusters and that the limiting shift is small with respect to those measured for the hydrogen-bonded modes. This observation suggests that the additional monomer units are progressively further removed from the free C-H stretch, consistent with a linear chain. The free C-H stretching frequency still depends (albeit weakly) on the addition of monomer units, even when the chain is seven molecules long, indicating that the free C-H stretch is still not completely isolated from what is going on at the other end of the chain. Unfortunately, the frequency shifts associated with the free C-H stretches are far too small to be calculated with sufficient accuracy using ab initio methods to aid in the assignment.

The situation is very different for the hydrogen-bonded C-H vibrational bands, for which the calculated frequency shifts are two orders of magnitude larger than those for the free stretch. The ab initio frequencies and intensities calculated by Karpfen (*6*) for linear chains of HCN up to the hexamer show that only one of the hydrogen-bonded C-H stretching vibrations is strongly infrared active in each complex. The calculated shifts for these intense bands (open triangles) are compared with the present experimental results (solid triangles) in Fig. 3B. For comparison, the ab initio (*6*) C-H stretching frequencies are shown as the solid squares in Fig. 3B for the corresponding cyclic complexes. The single cross in the figure gives the experimental frequency for the gas-phase cyclic trimer (*15*), which serves to provide a measure of the confidence level of the ab initio calculations.

To scan the large frequency range spanned by the hydrogen-bonded C-H stretches of the linear complexes efficiently, we tuned the laser in 300-MHz steps, which was sufficient to find these broad bands. Once found, the individual bands were rescanned by using continuous tuning, with and without the applied electric field. All of the bands (observed over a 200-cm^{-1} region to the red of the monomer) were strongly influenced by the electric field, indicating that they were associated with polar complexes. None of the nonpolar complexes observed in free jet expansions, including the cyclic trimer, was observed in the helium droplet spectrum. The pick-up cell dependence of the signals was again used to assign the cluster sizes. The agreement between the experimental and (linear chain) calculated frequencies is excellent (Fig. 3B), providing evidence in support of the assignment of these bands to linear chains, at least up to and including the hexamer. Although the shifts have not been calculated for larger clusters, the smoothness of the curve provides evidence that the other

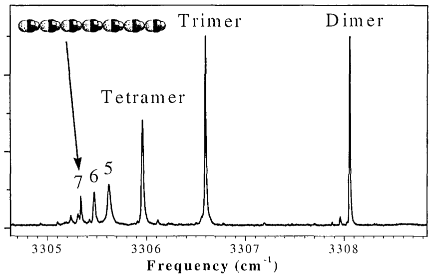


Fig. 2. Spectrum of the free C-H stretching region of the HCN polymer chains, showing clusters up to at least the heptamer. A linear heptamer chain is shown as an inset. This spectrum was obtained in the presence of a large electric field used to orient the polar chains within the helium droplet, thus collapsing the rotational band contours into a single peak for each cluster size.

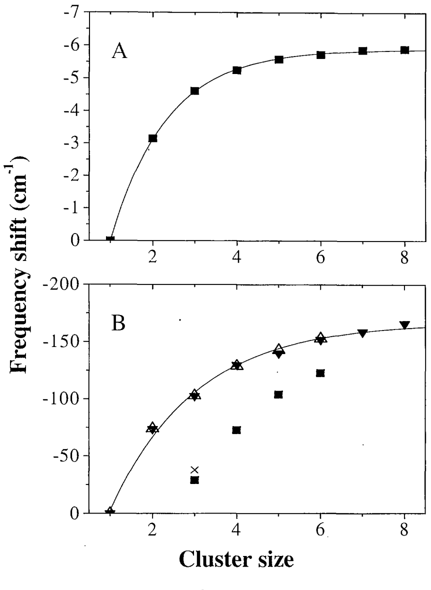


Fig. 3. Frequency shifts relative to the monomer for (**A**) the free C-H stretching vibrations and (**B**) the bonded C-H stretches. In (B), the experimental results (solid triangles) are compared with the ab initio (6) frequency shifts for the linear (open triangles) and cyclic (solid squares) complexes. The experimental value for the cyclic trimer (*15*) (cross) is also shown for comparison.

bands correspond to even longer chains. Although the calculated frequencies correspond to the chains in the gas phase, the comparison with the helium data is still valid because the helium interactions are weak and the resulting frequency shifts small. The smooth dependence of the frequency shifts on cluster size, the agreement with ab initio calculations, the observed polarity of the complexes, and the assignment of their size on the basis of the pick-up cell pressure dependence of the corresponding signals combine to give overwhelming evidence that the clusters observed in this study were indeed linear chains.

The observation of these extended linear chains is quite surprising given that condensation occurs at very low temperatures. The condensation energy will be very rapidly quenched by the liquid helium, thus one might expect that the molecules would freeze on contact and be trapped in a range of local minima on the potential energy surface, resulting in many different isomers. The fact that we only observed linear chains implies that the molecules only make contact in a head-to-tail configuration. At the low temperatures of the helium droplets, the dipole-dipole interaction between an HCN monomer and an already formed chain is sufficient at a distance of 3 nm to effectively cause the two to orient in their mutual fields. In this strong-interaction regime, the dipole-dipole interaction is not motionally averaged to $1/R^6$. Therefore, when the molecules approach one another they are already oriented in such a way as to favor the formation of linear chains. When the molecules finally aggregate, the condensation energy is presumably dissipated so rapidly by the liquid helium that the system becomes trapped in the linear configuration, even though the dispersion interactions favor the cyclic structures. The situation is similar to the production of a glassy or amorphous phase by rapid quenching. Thus, the separation of the distance scales associated with the dipolar ($1/R^3$) and dispersion ($1/R^6$) interactions is crucial to this very selective self-assembly.

Although the ab initio calculations and the free jet expansion data agree that the linear HCN chains do not correspond to the global minima on the gas-phase potential energy surface, an important question to consider is if this is also true in liquid helium. Certainly, in analogy with the denaturing of proteins, if the interaction between the chains and the solvent is strong enough, the open chains, which optimize such interactions, will become favored. Although detailed theoretical calculations will be needed to include the effects of the helium solvent, a simple calculation based on the relative excluded volumes for linear and cyclic complexes indicates that the helium solvation energy is not sufficient to energetically favor the linear chains. Thus, we conclude that the self-assembled chains observed here are fundamentally different from most self-assembled structures, in that they are not the minimum energy structures, nor are they in thermodynamic equilibrium.

One fundamental limit on the length of the chains that can be grown is the helium droplet diameter. A 10-molecule-long chain ($\sim$4 nm long) is about all that can fit within the present droplets once the evaporation of helium during the pick-up and condensation processes is taken into account. Another limitation for chain growth may have to do with the slow reorientation time associated with longer chains. As the moment of inertia of these long chains becomes very large, the reorientation needed to continue this self-assembly process may not be complete on the time scale for diffusion of the monomer unit. When this condition is reached, additional HCN monomers may attach to the sides of the chains, resulting in the formation of branched structures. Understanding these issues will be important for assessing the possibility and utility of extending this aggregation method to bulk liquid helium. Future studies should include examining the dependence of chain growth on the droplet size and attempting to grow long chains of water. In addition, more complex monomer units might be covalently linked after self-assembly, thus providing a new class of polar oligomers. Higher order moments (for example, quadrupole) could also potentially be used to self-assemble other structures.

References and Notes

1. J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gasses and Liquids* (Wiley, New York, 1965).
2. J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1992).
3. W. J. Dulmage and W. N. Lipscomb, *Acta Crystallogr.* **4**, 330 (1951).
4. M. Kofranek, A. Karpfen, H. Lischka, *Chem. Phys.* **113**, 53 (1987).
5. I. J. Kurnig, H. Lischka, A. Karpfen, *J. Chem. Phys.* **92**, 2469 (1990).
6. A. Karpfen, *ibid.* **100**, 13474 (1996).
7. K. K. Lehmann and G. Scoles, *Science* **279**, 2065 (1998).
8. M. Hartmann, R. E. Miller, J. P. Toennies, A. F. Vilesov, *Phys. Rev. Lett.* **75**, 1566 (1995).
9. S. Goyal, D. L. Schutt, G. Scoles, *ibid.* **69**, 933 (1992).
10. M. Hartmann, R. E. Miller, J. P. Toennies, A. F. Vilesov, *Science* **272**, 1631 (1996).
11. S. Grebenev, J. P. Toennies, A. F. Vilesov, *ibid.* **279**, 2083 (1998).
12. L. W. Buxton, E. J. Campbell, W. H. Flygare, *Chem. Phys.* **56**, 399 (1981).
13. K. W. Jucks and R. E. Miller, *J. Chem. Phys.* **88**, 6059 (1988).
14. D. S. Anex, E. R. Davidson, C. Douketis, G. E. Ewing, *ibid.* **92**, 2913 (1988).
15. K. W. Jucks and R. E. Miller, *ibid.* **88**, 2196 (1988).
16. R. E. Miller, *Science* **240**, 447 (1988).
17. P. A. Block, E. J. Bohac, R. E. Miller, *Phys. Rev. Lett.* **68**, 1303 (1992).
18. P. A. Block, K. W. Jucks, L. G. Pedersen, R. E. Miller, *Chem. Phys.* **139**, 15 (1989).
19. C. M. Lovejoy and D. J. Nesbitt, *J. Chem. Phys.* **87**, 1450 (1987).
20. R. E. Miller, unpublished data.
21. T. E. Gough, M. Mengel, P. A. Rowntree, G. Scoles, *J. Chem. Phys.* **83**, 4958 (1985).
22. M. Lewerenz, B. Schilling, J. P. Toennies, *ibid.* **102**, 8191 (1995).
23. This work was supported by the NSF (CHE-97-10026). We also acknowledge the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are grateful to E. Samulski and G. Scoles for several helpful discussions.

14 December 1998; accepted 8 February 1999

Epitaxial Cubic Gadolinium Oxide as a Dielectric for Gallium Arsenide Passivation

M. Hong,* J. Kwo, A. R. Kortan, J. P. Mannaerts, A. M. Sergent

Epitaxial growth of single-crystal gadolinium oxide dielectric thin films on gallium arsenide is reported. The gadolinium oxide film has a cubic structure isomorphic to manganese oxide and is (110)-oriented in single domain on the (100) gallium arsenide surface. The gadolinium oxide film has a dielectric constant of approximately 10, with low leakage current densities of about 10^{-9} to 10^{-10} amperes per square centimeter at zero bias. Typical breakdown field is 4 megavolts per centimeter for an oxide film 185 angstroms thick and 10 megavolts per centimeter for an oxide 45 angstroms thick. Both accumulation and inversion layers were observed in the gadolinium oxide–gallium arsenide metal oxide semiconductor diodes, using capacitance-voltage measurements. The ability to grow thin single-crystal oxide films on gallium arsenide with a low interfacial density of states has great potential impact on the electronic industry of compound semiconductors.

Effective passivation of III-V compound semiconductors (formed from elements of group III and V of the periodic table) finds many applications in photonic and electronic devices. Intensive efforts have been made over the past 30 years in searching for elec-