peratures and pressures (5). Trapping temperatures of fluid inclusions have been extensively determined by the observation of thin sections of a hydrothermal mineral as it is heated until the vapor and liquid observed at low temperature homogenizes into a single fluid. Such data generally show a wide range of temperatures in single deposits, and a few detailed studies show a complex temperature history during deposit formation (6). Chemical analyses of bulk solutions freed by laboratory crushing of hundreds of inclusions show that Na, Cl with lesser Ca, Mg, K, and sometimes major CO_2 are the major solutes. A few determinations of heavy metals in these bulk samples show tens of parts per million of Zn, Pb, Mn, and similar elements, but few direct determinations of heavy metal concentrations have been available. Changes of fluid chemistry with time remain a problem. Observations on layered veins and crystals, veins cross-cutting other veins, and similar features show that temperature, pressure, and chemical composition during hydrothermal precipitation vary in a highly complex manner, but most previous studies are only able to distinguish a few gross stages.

3) An especially informative contribution to genetic models has come from the study of modern geothermal systems (7–9). These systems are now believed to be modern analogs of ore-forming hydrothermal systems and sometimes deposit subeconomic- to ore-grade concentrations of, in particular, Hg, W, Ag, Au, and Sb (9). Data have been compiled on flow paths and rates for the hot solution along obvious faults and fractures, or through a myriad of small fractures or a porous permeable rock unit. Major flow along a restricted channel is generally favorable for the formation of a large high-grade deposit.

Quantitative models of the extraction of ore components from source rocks, of transport chemistry and flow dynamics, and of causes of deposition have been derived through the combination of thermodynamically calculated mineral stability and solubility, fluid inclusion temperature, and gross major solute data, isotopic data, and geothermal characteristics. However, the actual processes were more complex, and many assumptions were necessary in order to derive these models. Consequently, there remains an uncomfortable uncertainty about their accuracy.

Audétat *et al.* (1), using a new analytical method, resolve that uncertainty for one deposit and furnish a method applicable to many more. They used a laser drill to open individual inclusions directly into a mass spectrometer for analysis of the tiny (10^{-8} to 10^{-11} g) solution in the individual inclusions from a 27-step time sequence in a tin-bearing vein from Australia. Chemical concentrations in solution varied in the sequence by factors of more than 1000. The extremely high but variable temperatures of about 600°C, combined with ratios of different elements, imply precipitation of the early stages from several pulses of boiling magmatic fluid (>600°C). However, the detail of their data shows that the key to tin precipitation was the mixing of cool, dilute water with the hot solution during a late stage of the process. Analyses of associated vapor-rich inclusions, representing trapped vapor from the boiling solution, show that B and Cu were transported in this phase rather than by the liquid hydrothermal solution, as found elsewhere (10). The result is a reassuring confirmation, with much greater detail, of older models for the formation of tin deposits.

This analytical technique, applied to samples carefully studied by other methods, will allow a new level of understanding of temporal variations in hydrothermal chemistry and of the ore-depositing processes in the many types and variants of hydrothermal ores. Solubility of minor and trace elements at high temperature in real hydrothermal solutions can also be verified and extended.

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SUPERFLUID HELIUM

The Ultimate Spectroscopic Matrix?

K. K. Lehmann and G. Scoles

When chemists need to study unstable species, they resort to one of two methods. They can either produce and study the unstable species in a molecular beam or they can prepare and store the species in a frozen matrix (typically a film of solid argon deposited on a cold window inserted in a spectrometer). In the former method, perturbations are minimized, but synthetic flexibility is limited, whereas in matrix spectroscopy, the opposite is true: many different species can be prepared (*1*), but perturbations from the matrix that cause inhomogeneous broadening can hardly be avoided. In spite of the limitations, both methods have had a dramatic impact on the development of modern chemistry. On page 2083 of this issue, Grebenev *et al.* (*2*) report results that disentangle an important unresolved question that arises when these two methods are combined in what is called helium cluster beam isolation spectroscopy.

In fact, one way to minimize matrix-induced perturbations is to use solid or liquid helium as the host matrix. The main problem here is the injection of the condensable sample into the extremely cold matrix without causing aggregation or condensation on the container walls. This is normally achieved by laser ablation of a sample located in or near the solid or liquid helium matrix (*3*). Here too, however, sample aggregation and stability remain sources of problems.

In recent years, a synthesis of molecular beams with matrix spectroscopy has been developed that appears to contain the solution to the problems described above. In this method (see figure), a beam of large noble gas clusters, each containing 10^3 to 10^5 atoms, picks up in flight (without being deflected) one or more atoms or molecules, which can then be studied downstream by laser spectroscopy (*4*). This technique has grown in importance since being extended to liquid helium clusters (*5*) and especially since the group of Toennies in Göttingen showed that a large variety of impurity molecules inside ^{4}He clusters give spectra indicative of free molecular rotation instead of the diffusive rotational or librational motions expected for condensed-phase molecules (*6*). Although it was previously observed that light molecules with weak anisotropic interactions (such as H_2 or CH_4) could freely rotate in the condensed phase, this was the first time that heavy molecules with high anisotropy, such as the dimer of SF_6, were observed to freely rotate in a liquid medium, albeit with an increased moment of inertia (*7*). The possibility of resolving rotational molecular spectra in superfluid helium clusters couples the syn-

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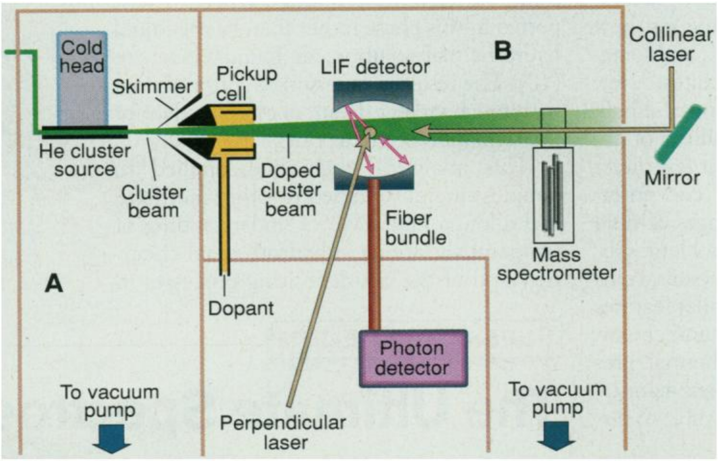
thetic flexibility of matrix deposition with the structural sensitivity of rotational-state–resolved spectroscopy and propels this technique to the forefront of the methods available for the study of unstable species. Furthermore, it allows for the study of superfluidity at the nanoscale level, an interesting subject in condensed-matter physics with a separate fundamental interest in itself.

Although it is natural to assume that free molecular rotation in liquid ^{4}He clusters is a consequence of their superfluid character (*8*), it cannot immediately be ruled out that it is instead a result of the cold, weakly interacting fluid environment where the zero-point motion of the helium atoms is likely to be important. The obvious way to distinguish between these two possibilities is to take a spectrum of the same molecule in both ^{4}He and ^{3}He clusters. The latter are expected to be of lower density—and thus, more weakly interacting and colder—but not to show superfluidity. It is just such an experiment that Grebenev, Toennies, and Vilesov report in this issue (*2*).



Making clusters. Configuration of the helium-cluster–isolation spectrometer. A beam of large helium clusters is formed in chamber A, becomes doped in the pickup cell, and is probed by a perpendicular or coaxial laser in chamber B. Laser-induced fluorescence (LIF) or beam depletion can be used to detect spectroscopic transitions. For the synthesis of unusual compounds, more than one pickup cell can be used, and the gases flowing through them can be the products of a discharge or pyrolytic decomposition.

The authors find that for pure ^{3}He clusters, the vibrational spectrum of an embedded OCS molecule shows no rotational structure, giving instead a band shape that the authors interpret as due to rotational diffusion with a lifetime of 50 ps. In contrast, the spectrum of OCS in pure ^{4}He clusters gives the spectral structure expected for a linear molecule. This result unambiguously demonstrates that the free molecular rotation is a consequence of the boson nature of ^{4}He atoms and, thus, is likely a result of superfluidity. The authors then added a known mean level of ^{4}He impurity into the otherwise pure ^{3}He clusters. Because of the difference in zero-point energy, it was expected that these ^{4}He impurities would migrate to and surround the OCS molecule. When the mean number of ^{4}He impurity atoms neared 60 (corresponding to about two solvation shells), the OCS vibrational spectrum took on a structure indicative of free molecular rotation.

One can appreciate the beautiful elegance displayed and the technical challenge posed by the experiment of the Göttingen group, considering that its successful completion required the use of ^{3}He containing less than 1 part in 10^4 of ^{4}He and the detection of infrared spectroscopic transitions in an extremely thin optical target. The fact that free rotation is recovered when two layers of ^{4}He "condense" around the OCS molecule can be correlated with the finding that on a solid surface, approximately two layers of ^{4}He are needed before robust signs of film superfluidity are obtained (*9*). Although the thickness of this "inert" layer changes with the composition and the structure of the substrate (*10*), we find the above correlation rather fascinating and probably not coincidental.

The results presented by Grebenev *et al.* (*2*) resolve a fundamental question of helium-cluster–isolation spectroscopy and, equally importantly, give the first experimental hints of the minimum number of atoms required for superfluidity. Several other questions remain, including understanding the origin of the measured effective rotational constants. For different molecules, these values vary from only slightly smaller than that observed for the free molecule in gas phase to a reduction as large as a factor of 5. In their report, Grebenev *et al.* propose that the dominant contribution to the increase in the moment of inertia arises from a "normal" fluid fraction of the liquid that rotates rigidly with the impurity molecule (*2*). However, it is not easy to find a way to define the normal density of the liquid as a function of distance from the impurity (a problem that arises also in the study of superfluid films). Theoretical calculations on SF_6 in ^{4}He clusters have demonstrated that even the first ^{4}He solvation shell, which is strongly attracted to the impurity, participates in the long-range Feynmann interchanges that are indicative of the long-range correlations that lead to superfluidity (*11*). Furthermore, the Landau model treats the "normal" fluid as a set of quasiparticle excitations of the superfluid ground state. Estimates of the excitation energies based on the liquid-drop model indicate, however, that a cluster of 60 ^{4}He atoms cannot have any internal excitations thermally excited at 0.15 K, which is the temperature stabilized by the dominant presence of ^{3}He in the cluster. Thus, one would expect a negligible normal fluid contribution.

A nice, large window has been opened simultaneously on two seemingly unrelated and not totally understood subjects: the study of quantum phase transitions in constrained geometries, and the pursuit of metastability in the chemical world. Although it would not be unusual if, with the introduction into chemistry of new physical methods, both disciplines end up making progress, this particular case is unusual in that the clarification of a fundamental physics question is coupled to the utilization of a method of great chemical promise. To prove with an example that the potential for chemistry is indeed large, consider the fact that one of the main properties of liquid ^{4}He is its inertness with respect to both nuclear and electronic spin relaxation. Indeed, it has already been proven that in ^{4}He clusters, high-spin species of extremely small metastability can be prepared and can be used as precursors to unusual chemical events (*12*).

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