

ELEMENTAL MERCURY

State oddity

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Elements of any given group in the periodic table generally have properties that are not too dissimilar, but notable exceptions exist; mercury is one such curiosity. Among other oddities, it is a liquid at room temperature

— a particularly dense one — when all other metallic elements are solids. It has long been suspected that the peculiar characteristics of mercury arise from relativistic effects. In an international collaboration between France, New Zealand and Germany, Florent Calvo, Peter Schwerdtfeger and co-workers have now shown that this is indeed the case.

Including relativity in calculations means taking into account the fact that objects become heavier as they move faster. The resulting effects are usually negligible for light atoms, but for those with heavier nuclei — which exhibit larger electrostatic forces — inner-shell electrons reach relativistic speeds. These effects cause atomic orbitals to contract or expand, and this alters the bonding strength between atoms. Calvo, Schwerdtfeger and colleagues have now devised Monte Carlo simulations using a quantum diatomics-in-molecules method, derived from relativistic calculations for Hg_2 , to model the interactions between mercury atoms.

Heat-capacity plots were calculated for mercury clusters of different sizes

(comprising 13, 19 or 55 atoms) and bulk mercury, with and without taking into account relativistic effects. Significant differences arose between the two scenarios, albeit not in a manner proportional to cluster size. On inclusion of relativity, the structures of the clusters were distorted and their melting points shifted — higher for Hg_{13} and Hg_{55} , but lower for Hg_{19} . These findings are consistent with complex many-body interactions that are known to occur in mercury: for clusters of increasing sizes, Hg–Hg bonding changes from van der Waals to covalent to metallic.

For the bulk material, accounting for relativity caused the calculated melting point to drop from 82 to -23 °C, much closer to the experimental value (-39 °C), and is consistent with mercury's liquidity at room temperature. The predicted density also shifted to a value very close to the experimental one. Further calculations revealed that the relativistic effects mostly arise from many-body contributions rather than spin–orbit coupling effects. AP

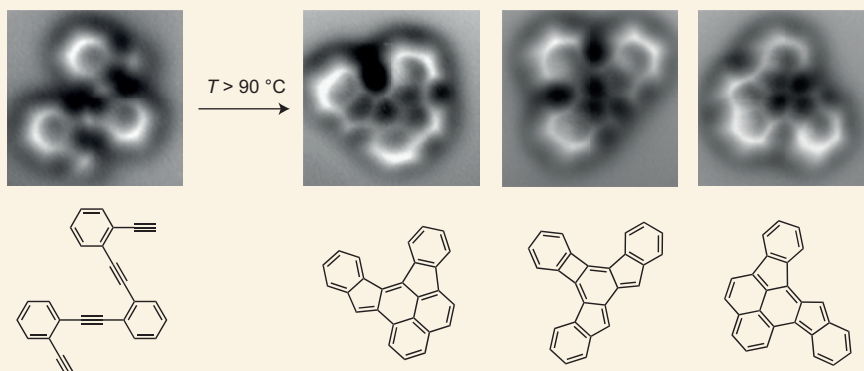
SCANNING PROBE MICROSCOPY

Structural snapshots

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Products of chemical reactions involving organic compounds are typically characterized by analysing bulk samples with techniques such as NMR spectroscopy, mass spectrometry and — if you are lucky enough to get good-quality crystals — X-ray crystallography. Advances in scanning probe microscopies have, however, reached a point where it is possible to image single molecules resting on a surface and, in some cases, can reveal the precise bonding arrangement of the constituent atoms. Although it would be impractical to determine the structure of every single product molecule from a given reaction in this way, direct imaging can potentially provide structural information that may be difficult to glean from other techniques.

Now, a team of researchers from the USA and Spain led by Michael Crommie and Felix Fischer have taken 'before' and 'after' pictures of individual oligo(phenylethynylene) molecules that undergo various thermally activated isomerization reactions on a silver surface. Images of the starting material and products were captured with a scanning tunnelling microscope, and the different



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blob-like features present on the surface following the reaction suggested that a range of products are formed. Higher-resolution images obtained using non-contact atomic force microscopy — in which the tip of the microscope is functionalized with a single CO molecule — revealed the different covalent-bond frameworks (pictured) of the molecules formed in a series of cyclization reactions.

For the two most abundant products, Crommie, Fischer and co-workers investigated possible reaction pathways with density functional theory calculations. The

starting material can be considered to be made up of overlapping enediyne systems that can undergo a range of different reactions, including Bergman cyclizations and radical shifts. For each reaction, it was found that the initial cyclization process presents the highest energy barrier and so is the rate-determining step. The different products arise from the possibility of cyclization reactions giving 4-, 5- or 6-membered rings, with 5-membered rings seemingly more favoured under the experimental conditions used in this study than is usually the case. SC