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and subsequent adiabatic expansion from 2 to 3, (iii) establishment of thermal contact with the entropy sink to effect isothermal compression from 3 to 4 at temperature $T_e$, and (iv) breaking of thermal contact and continuance of adiabatic compression from 4 to 1.

We define the efficiency of the photon-Carnot engine as $\eta = (Q_{in} - Q_{out})/Q_{in} = (T_b S_{12} + T_e S_{34} - kT_e S_{12}) / (kT_e S_{12})$. In the high-temperature limit ($kT_e \gg k\Omega$) and small expansion ($\Delta \Omega = \Omega_1 - \Omega_2 \ll \Omega$) limits, $S_{net} = S_{34} - k\Delta \Omega / \Omega$.

Engine efficiency, when fueled by regular thermal atoms, is then given by $\eta = 1 + (T_b S_{12}) / T_e S_{12} = 1 - T_b / T_e$. However, when the radiation working fluid is heated by phase-coherent atoms, $T_b \to T_0$, and the Carnot efficiency is given by

$$\eta_c = 1 - \frac{T_b}{T_0} \left( \frac{\delta}{\pi} \left( \frac{\Omega}{\Delta} \right)^{\frac{1}{2}} \right)$$

where $\delta = 3\pi n_b \omega / 2$. Hence, $\eta_c > \eta$ when, for example, $\delta = \pi$.

We see from Eq. 7 that when $T_b = T_e$ and $\eta = 3\pi n_b \omega / 4$, the photon engine produces work from a single heat bath. The net work produced, when $T_b = T_e$ is

$$W_{net} = \eta_c T_e S_{12} \approx \frac{\delta}{\pi} \frac{h \omega}{kT} \frac{\Delta \Omega}{\Omega} \frac{\Omega}{\Omega}$$

where the “Rabi flopping” angle $\theta_0$ is the (small) tipping angle defined below.

The atomic coherence can be generated, for example, by passage of the atoms through a microwave field $\omega (I)$, which may be approximated by a coherent state $|\alpha\rangle$ that has a mean photon number $N_\alpha = |\alpha|^2$. If the resonant atom-field coupling frequency is $g_\alpha$, and the interaction time is $\tau_\alpha$, then $\rho_{bc} = \exp (i\alpha / \hbar) \rho_{bc} / 3kT_\alpha$, where $\alpha = g_\alpha \tau_\alpha |\alpha|^2$ and we have taken the high-temperature limit $\rho_{bc} = \rho_{bb} \approx 3kT\omega / 4\Omega$. We may then write $5\pi n_b \omega / 2 = \rho_{bc} / 3kT$. Hence if we take reasonable values; $\delta = 0.1$, $\omega / \Omega = 0.1$, and $\hbar \approx 10^{-11}$, we find $|\alpha|^2 \approx 3 \times 10^{-6}$. Hence, for $|\rho_{bc}|$ of order $10^{-5}$, efficiencies $\eta_c$ are of a few percent ($10, 11$) even though $T_b \to T_e$.

Heatings governed by $\Delta$ are unimportant in determining the temperature of the field. The atomic density matrix after microwave preparation is given by Eq. 6, where $\Delta \sim \omega / h \omega / kT$ is higher order in $\theta_0$. Furthermore, the effects of $\Delta$ cancel out as can be seen in Eq. 5 and if $\theta_0$ is replaced with $P_c + \Delta$ and $P_e$ is replaced with $P_c - \Delta$. Hence, the physics is contained in $P_c$ and $P_b$.

We can estimate the microwave energy, $W_{mic}$ necessary to produce coherence between $b$ and $c$, given the preceding microscopic model of our QHE (10, 11). The important point is that we find $W_{mic} \approx 5W_{net}$, i.e., $W_{mic} > W_{net}$ in the present QHE.

The quantum thermodynamics of systems slightly out of equilibrium is an area of current interest (22). In the particular form of nonequilibrium considered here, quantum coherence, the phase $\phi$ is found to be a demon-esque control parameter that allows work to be extracted from a single bath. The total system entropy is constantly increasing, and the physics behind the second law is not violated. However, quantum coherence does allow certain features of engine operation beyond the classical limit.

References and Notes

3. Reviews of LWI are to be found in (12–14). For the quantum theory of a micromaser, see (34).
13. M.O.S. wishes to thank N. Ramsey for many stimulating and helpful discussions. This paper is an outgrowth of QHE discussions with D. Kleppner, F. Narducci, T. Opatrny, and N. Ramsey at the TAMU-QNR 2001 workshop. Useful conversations on the subject of radiation thermodynamics with G. Baym, P. Martin, P. Meystre, and W. Phillips are gratefully acknowledged, as are helpful discussions on the present manuscript with K. Annamalai, K. Chapman, R. Curl, D. Depatie, B.-G. Englert, E. Fry, R. Hulet, C. Joachain, K. Kapale, V. Kurchanovs, S. Lloyd, A. Muthukrishnan, T. Opatrny, M. Pillof, Y. Rostovtsev, Z. Sariyanni, and G. Sussmann. We thank R. Haden, the Texas Engineering Experiment Station, the Office of Naval Research, the DARPA-QUEST program, and the Welch Foundation for supporting this research.
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Au$_{20}$: A Tetrahedral Cluster

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Photoelectron spectroscopy revealed that a 20-atom gold cluster has an extremely large energy gap, which is even greater than that of C$_{60}$, and an electron affinity comparable with that of C$_{60}$. This observation suggests that the Au$_{20}$ cluster should be highly stable and chemically inert. Using relativistic density functional calculations, we found that Au$_{20}$ possesses a tetrahedral structure, which is a fragment of the face-centered cubic lattice of bulk gold with a small structural relaxation. Au$_{20}$ is thus a unique molecule with atomic packing similar to that of bulk gold but with very different properties.
Gold is undoubtedly an important material, and small clusters of gold have also attracted great attention. Although gold colloids have been used for centuries to stain glass (9), more recently it has been shown that gold clusters have unusual catalytic properties for selective oxidation of CO (4–7), are oxidation-resistant (8), enable selective binding of DNA (9), and have potential applications in nanoelectronics (10–16). Small Au cluster cations possess planar structures up to Au$_{12}^+$ (17), whereas Au cluster anions are planar up to at least Au$_{12}^-$ (18, 19). We have probed the electronic and geometrical structures of small Au clusters using anion photoelectron spectroscopy (PES) and computer simulation. The improved instrumental resolution (20) and the ability to produce cold clusters (21) enabled us to obtain considerably more detailed electronic structure information than was previously possible (22). We found that 20-atom gold clusters exhibit a HOMO-LUMO gap even greater than that of C$_{60}$. Relativistic density functional calculations predict that Au$_{20}$ possesses a tetrahedral geometry, similar to that of a fragment of the bulk face-centered cubic (fcc) crystal of gold. Details of our PES apparatus have been described elsewhere (20, 23). Small Au$_n^-$ clusters were produced by means of laser vaporization of a pure gold target with a helium carrier gas and were mass-analyzed with time-of-flight mass spectrometry. Pure Au$_{20}^-$ clusters were selected and decelerated before photodetachment by a pulsed laser beam. Figure 1 shows the PES spectra of Au$_{20}$ at three photon energies. The 193-nm spectrum of Au$_{20}$ (Fig. 1C) displays a weak peak around 2.7 eV labeled X, followed by a large energy gap and more discrete transitions at higher binding energies (A, B, C . . .). This spectral pattern suggests that neutral Au$_{20}$ is a closed-shell molecule with a large HOMO-LUMO gap.

The electron that enters the LUMO of Au$_{20}$ is removed upon photodetachment of the anion, yielding the neutral ground state (X in Fig. 1). The feature A corresponds to the lowest triplet excited state of the neutral. Thus, the A-X separation, measured to be 1.77 eV (Fig. 1B), represents the excitation energy of the first triplet excited state of neutral Au$_{20}$ but is also an approximate experimental measure of the HOMO-LUMO gap. This energy gap in Au$_{20}$ is very large, about 0.2 eV greater than that in C$_{60}$ (1.57 eV) (24) (Fig. 2). However, electron signals were observed in the HOMO-LUMO gap region in the 266-nm spectrum (Fig. 1B), owing to autodetachment, as a result of a photoexcited Au$_{20}^-$ upon absorption of a 266-nm photon. Similar autodetachment signals were also observed previously in C$_{60}$ (24). The 355-nm spectrum of Au$_{20}$ revealed a very sharp peak at the ground state transition (autodetachment signals were also observed at this detachment energy), suggesting that there is very little geometry change between the ground state of Au$_{20}$ and neutral Au$_{20}$. This is different from C$_{60}^-$, whose PES spectra exhibit vibrational features due to structural distortions of the anion and ground state (25). The 355-nm spectrum yielded a vertical detachment energy of 2.751 ± 0.010 eV and an adiabatic detachment energy of 2.745 ± 0.015 eV for Au$_{20}$.

The latter is the electron affinity (EA) of Au$_{20}$: a measure of how tightly the cluster can bind an electron. The EA of Au$_{20}$ is higher than that of C$_{60}$ (2.689 eV) (24), so Au$_{20}$ is even more electron-repulsive than C$_{60}$.

According to the electron shell model (26), Au$_{20}$ with 20 valence electrons should represent a major shell closing. What is surprising is the magnitude of the HOMO-LUMO gap. With the exception of Au$_3$ and Au$_{15}$, the HOMO-LUMO gap observed for Au$_{20}$ is the largest among all known coinage-metal clusters (22). It is also larger than that observed in the recently discovered 18-electron icosahedral W@Au$_{12}$ cluster (27, 28).

The large HOMO-LUMO gap suggests that Au$_{20}$ should be very inert and may possess a highly symmetric geometry. To elucidate its structure and bonding, we carried out an extensive structural search for neutral and negatively charged Au$_{20}$, using relativistic density functional calculations (29–33). We started from the highest symmetry possible [the Platonic dodecahedron with icosahedral ($I_h$) symmetry and octahedron with octahedral ($O_h$) symmetry] to their various important subgroups, as well as the ring and bowl structures known for C$_{60}$ (34) (Table 1 and Fig. 3). We also tested a capped decahedron ($C_{2v}$) structure (Fig. 3C) and an amorphous ($C_{3v}$) structure (Fig. 3B), which were found as “global” minima in previous calculations (35, 36). The $I_h$ and $O_h$ Au$_{20}$ structures are open-shell structures and would be subject to Jahn–Teller distortions of the anion ground state (27).

Fig. 1. Photoelectron spectra of Au$_{20}^-$. (A) At 355 nm [3.496 eV]. (B) At 266 nm [4.661 eV]. (C) At 193 nm [6.424 eV]. The 355- and 266-nm photons were from a Nd–yttrium-aluminum-garnet laser, and the 193-nm photons were from an ArF excimer laser. Photoelectrons were analyzed with a magnetic bottle–type photoelectron spectrometer and calibrated using the known spectrum of Rh$. The electron kinetic energy resolution was about 2.5%, that is, ~25 meV for 1-eV electrons.

Fig. 2. Comparison of the photoelectron spectra of Au$_{20}^-$ with those of C$_{60}^-$. (A) The 266-nm spectrum of C$_{60}^-$. “AD” stands for autodetachment signals. (B) The 266-nm spectrum of Au$_{20}^-$. (C) The 193-nm spectrum of C$_{60}^-$. (D) The 193-nm spectrum of Au$_{20}^-$. C$_{60}^-$ data are from (24).
The linear chain is highly unstable, with small HOMO-LUMO gaps (Table 1). Because smaller Au21– (n < 13 atoms) clusters prefer planar geometries (18, 19), we also calculated a planar Au20 structure (Fig. 3D), as well as a linear Au20 chain, which has recently been formed on a NiAl surface and studied with scanning tunneling microscopy (STM) (20). The calculated EA for the lowest triplet state (3A1g) is 1.777 eV, in close agreement with the experimentally determined value of 1.77 eV. The excellent agreement between the calculated EA and excitation energy and the experimental measurements can probably be attributed to the fact that very little change in geometry exists between the anion ground state and the neutral ground and excited states, and it confirms unequivocally that Au20 possesses a tetrahedral structure.

Further confirmation of the Td structure is provided by the theoretical detachment spectrum (Fig. 4), which shows that major PES features are all well reproduced in the simulated spectrum for Td Au20 (38).

Tetrahedral Au20 is a small piece of bulk gold with a small relaxation. Each of the four faces represents a (111) surface of fcc gold. It has a very high surface area (all the atoms are on the cluster surface) and a large fraction of corner sites with low coordination. The three different kinds of atoms in the Td structure, 4 at the apexes, 4 at the center of each face, and 12 along the edges (Fig. 3A), have different covalent radii. The three different kinds of atoms in the Td structure, 4 at the apexes, 4 at the center of each face, and 12 along the edges (Fig. 3A), have different covalent radii.

To facilitate comparison with experimental results, we also optimized the geometries of the anions for all the isomers (Table 1). Consistent with the experiment, very little structural change was observed upon electron addition to Td Au20; the calculated detachment transition energies with the experimental measurement (Table 1).

Because the X-A gap (Fig. 1) represents the excitation energy of the lowest triplet excited state, we also calculated this quantity for Td Au20. The calculated excitation energy for the lowest triplet state (3A1g) is 1.777 eV, in close agreement with the experimentally determined value of 1.77 eV. The excellent agreement between the calculated EA and excitation energy and the experimental measurements can probably be attributed to the fact that very little change in geometry exists between the anion ground state and the neutral ground and excited states, and it confirms unequivocally that Au20 possesses a tetrahedral structure. Further confirmation of the Td structure is provided by the theoretical detachment spectrum (Fig. 4), which shows that major PES features are all well reproduced in the simulated spectrum for Td Au20 (38).

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Tetrahedral Au20 is a small piece of bulk gold with a small relaxation. Each of the four faces represents a (111) surface of fcc gold. It has a very high surface area (all the atoms are on the cluster surface) and a large fraction of corner sites with low coordination. The three different kinds of atoms in the Td structure, 4 at the apexes, 4 at the center of each face, and 12 along the edges (Fig. 3A), have different coordination environments and may provide ideal surface sites to bind different molecules for catalysis (such as CO, O2, and CO2) (39). The large HOMO-LUMO gap of Au20 suggests that it is a highly inert and stable molecule and may possess novel chemical and physical properties; its unique tetrahedral structure makes Au20 an ideal model for gold surfaces.
Carbon Tunneling from a Single Quantum State

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We observed ring expansion of 1-methylcyclobutylfluorocarbene at 8 kelvin, a reaction that involves carbon tunneling. The measured rate constants were $4 \times 10^{-6}$ per second in nitrogen and $4 \times 10^{-5}$ per second in argon. Calculations indicated that at this temperature the reaction proceeds from a single quantum state of the reactant so that the computed rate constant has achieved a temperature-independent limit. According to calculations, the tunneling contribution to the rate is 152 orders of magnitude greater than the contribution from passage over the barrier. We discuss environmental effects of the solid-state inert-gas matrix on the reaction rate.

Quantum mechanical tunneling frequently plays an important role in reactions in which a hydrogen atom (H), proton (2 H), or hydride ion (3 H) is transferred. In most organic reactions, motion of carbon is also part of the reaction coordinate, and kinetic isotope effects are consistent with a contribution from carbon motion in some tunneling reactions. However, evidence for tunneling in reactions that are dominated by carbon motion is rare.

One reaction in which there is good experimental and theoretical evidence for carbon tunneling is the automerization of 1,3-cyclobutadiene ($5 \rightarrow 7$). In this reaction, the carbons each need to move only about 0.1 Å, resulting in a thin barrier that favors tunneling (5). This reaction has been observed at 25 K in an argon matrix (6), and tunneling still occurs, despite the solid-state environment of the reactant (6).

A few other transformations that involve the making or breaking of C–C or C–H bonds have been observed at very low temperatures, where there is unlikely to be thermal energy sufficient to allow molecules to surmount any but the most miniscule barriers to reaction (9–11). The finite rates observed in these reactions suggest that carbon tunneling may be involved. However, the interpretation of these experiments is complicated because in each case, the rate-determining step apparently involves intersystem crossing to an electronic state from which the observed reaction is likely to occur without a barrier.

Tunneling by carbon might play a role in 1,2-shifts in singlet carbocycles. The distance between the carbene center and the carbon that migrates to it changes by about 1 Å in these exothermic rearrangements. However, tunneling appears to make only minor contributions to the rates of ring expansions of cyclopolyhalocarbenes in liquid solution at 298 K (12). Nevertheless, rearrangements of cyclobutylhalocarbenes to 1-halocyclopentenes are expected to have lower barriers, because in these reactions there is less hyperconjugative stabilization of the reactants and more relief of ring strain in the products than in the ring expansions of cyclopolyhalocarbenes. Indeed, cyclobutylhalocarbenes are shorter-lived in solution at room temperature than are the corresponding cyclopolyhalocarbenes (13, 14).

Here, we report an experimental and com-