

of the circle shown in Fig. 3A. However, because the tip would have to be moved from one cluster position to the next, controlled by the microprocessor, this method would be much slower (approximately by a factor of 10) than cluster production during scanning. Although 400 Cu clusters were produced during a very short time, there was no indication of Cu depletion at the tip as all clusters are nearly identical in size (height $h = 0.6$ nm, FWHM = 3.5 nm). This result suggests that the Cu reservoir at the tip is continuously refilled as a result of permanent Cu deposition from solution (tip potential $E_{\text{tip}} = -30$ mV versus Cu/Cu^{2+}).

Continuous structures can also be generated with microprocessor-controlled cluster formation by placing the Cu clusters very close together so that they can contact each other. For example, we have produced nanometer-sized "conducting wires" with a FWHM of 3 to 4 nm and a length of several hundred nanometers on Au(111) (19).

In addition to precisely positioning individual Cu clusters with identical heights, it is also possible with this system to vary the size of the deposited clusters in a controlled manner within certain limits. This can be done by varying the extent of the tip approach with the external z pulse, which controls the amount of Cu transferred from the tip to the Au surface (Fig. 5, A and B). In general, the cluster height increases with increasing z -pulse height,

but, above a tip displacement of $\Delta z \approx 1.2$ nm, the cluster height did not increase further and holes appeared in the surface instead. This result suggests that the tip displacement became too large and the tip struck the substrate.

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13. The potentials of tip and sample could be controlled independent of each other by means of a bipotentiostat. The tips used for modification and imaging were made from a Pt/Ir wire (80:20) by electrochemical etching and were subsequently coated with Apizeon wax to reduce the area in contact with the electrolyte, thus reducing the faradaic current at the tip to <0.1 nA. The working electrodes were evaporated Au films on Robax AF45 glass (Berliner Glas KG), which, after proper flame-annealing in an H_2 -air flame, had (111) surfaces whose quality was similar to that of Au(111) single crystals.
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19. We are currently examining the possibility of the formation of such structures on semiconducting substrates, which would be of greater technological interest than deposition on metals (D. M. Kolb *et al.*, in preparation).
20. Supported by the Deutsche Forschungsgemeinschaft through grant Ko 576/10-2. We thank R. Liske for developing the microprocessing unit.

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Five-Coordinate Hydrogen: Neutron Diffraction Analysis of the Hydrido Cluster Complex $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$

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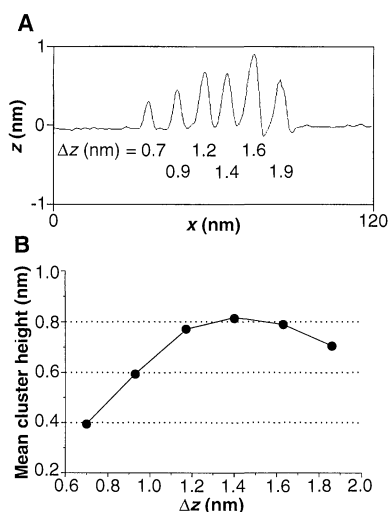


Fig. 5. (A) Cross section of six Cu clusters in a row on Au(111) in 0.05 M H_2SO_4 + 1 mM CuSO_4 , which demonstrates the variation of cluster height with the z -pulse height. The corresponding tip displacement Δz is shown in the figure. Pulse duration of $\Delta t = 10$ ms; $E_{\text{sample}} = +10$ mV; $E_{\text{tip}} = -50$ mV; $I_t = 2$ nA. (B) Mean cluster height, as derived from 15 experiments, as a function of the tip displacement Δz used to generate the Cu clusters. The dotted lines indicate the height of a Cu monolayer. $E_{\text{sample}} = +10$ mV; $E_{\text{tip}} = -50$ mV; $I_t = 2$ nA.

Pentacoordinate hydrogen atoms were identified by single-crystal neutron diffraction analysis of $[\text{N}(\text{CH}_3)_4]_3[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]$. The hydrogen atoms are located in square pyramidal cavities of the Rh_{13} cluster, in positions almost coplanar with the Rh_4 faces on the surface of the cluster. They are slightly displaced inward, toward the central rhodium atom of the cluster, with average H–Rh(central) and H–Rh(surface) distances of 1.84(2) and 1.97(2) angstroms, respectively. This result shows that hydrogen, which normally forms only one bond, can be attached to five other atoms simultaneously in a large metal cluster.

In the late 1970s, it was shown by neutron diffraction (1–3) that H atoms could exist in the interstitial sites of metal cluster compounds such as $[\text{HCo}_6(\text{CO})_{15}]^-$, $[\text{HRu}_6(\text{CO})_{18}]^-$, $[\text{HNi}_{12}(\text{CO})_{21}]^{3-}$, and $[\text{H}_2\text{Ni}_{12}(\text{CO})_{21}]^{2-}$. The H atoms were found to be

either six-coordinate ($\mu_6\text{-H}$), located at the centers of metal octahedra (1, 2), or in triply bridging positions ($\mu_3\text{-H}$) on the interior faces of metal octahedral cavities (3). Here we report an example of pentacoordinate hydrogen ($\mu_5\text{-H}$) found in the square pyramidal cavities of the cluster complex $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$.

The $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$ anion, first reported in 1975 (4), is a member of a family of clusters, $[\text{H}_x\text{Rh}_{13}(\text{CO})_{24}]^{(5-x)-}$ ($x = 1$ to 4), whose members are interconvertible by means of a series of acid-base equilibria (4–9). The Na salt of the title anion was prepared by refluxing a mixture of $\text{Rh}_4(\text{CO})_{12}$ and NaOH in isopropanol under an atmosphere of H_2 , followed by addition of Na_2CO_3 (8). It was

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then converted to the tetramethylammonium salt by metathesis with $[\text{N}(\text{CH}_3)_4]\text{Cl}$. Slow recrystallization from a mixture of isopropanol and methyl ethyl ketone yielded crystals of $[\text{N}(\text{CH}_3)_4]_3[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}] \cdot (\text{CH}_3\text{COC}_2\text{H}_5)$ just large enough for neutron diffraction. A small crystal was first used for a preliminary x-ray diffraction analysis (10) to obtain the atomic positions of the non-H atoms. Neutron diffraction data were collected at 15 K on a crystal with volume 1.8 mm^3 over an 11-week period at the Brookhaven High-Flux Beam Reactor (11–13). Difference-Fourier maps, phased by the non-H positions, readily revealed the two hydridic peaks, as well as those corresponding to the H atoms of the tetramethylammonium ions and the methyl ethyl ketone solvate molecule. The structure was refined to a final agreement factor of $R(F) = 0.12$ for 2678 reflections with $I > 3\sigma(I)$ (14).

Molecular plots of the $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$ anion (Fig. 1) and its H_2Rh_{13} core (Fig. 2) show that the two H atoms are located in two of the six square pyramidal cavities of the cluster (Fig. 3). The two hydridic atoms are almost coplanar with the four basal (surface) Rh atoms of each square pyramidal cavity, slightly displaced toward the central atom of the cluster, Rh13 (Fig. 2B). In both cases, the axial Rh13–H distance (see Table 1) is slightly shorter [average, $1.84(2) \text{ \AA}$] than the four surface Rh–H distances [average, $1.97(2) \text{ \AA}$] (the number in parentheses is the error in the last digit).

The mean Rh–H distance (averaged over all 10 bond lengths) is $1.95(2) \text{ \AA}$, which, given the average covalent radius of $1.35 \text{ \AA}$ for Rh [taken as half of the Rh–Rh

distance in Rh metal (15)], leads to an effective radius for H of $0.60 \text{ \AA}$ in $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$. This radius is comparable to the value of $0.53 \text{ \AA}$ estimated (1) for the radius of H in $[\text{HCo}_6(\text{CO})_{15}]^-$ but is significantly larger than the normal H covalent radius of $0.37 \text{ \AA}$ (half of the H–H distance in H_2). This result suggests that there is in fact an excess of space for the H atoms in the square pyramidal cavities of the Rh_{13} cluster. Compared to other Rh–H distances accurately characterized by neutron diffraction (Table 2), one sees a steady increase of Rh–H distance with increasing H coordination number, an observation that may reflect a decrease in metal–H bond order along the series $\mu_1\text{-H} > \mu_2\text{-H} > \mu_3\text{-H} > \mu_5\text{-H}$ (16).

A legitimate question to ask at this point is why the H atoms are not disordered. In principle, the two H atoms could be delocalized over the six available square pyramidal sites, leading to a net occupancy of one-third of a H atom in each cavity. However, this was not the case, because the

arrangement of bridging CO groups (Fig. 1) effectively reduces the point group symmetry of the Rh_{13} cluster from D_{3h} to C_s and creates four inequivalent types of Rh_5 cavities. In their original x-ray diffraction studies on $[\text{PPh}_3(\text{CH}_2\text{Ph})]_3[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]$ (Ph = C_6H_5) and $[(\text{PPh}_3)_2\text{N}]_2[\text{H}_3\text{Rh}_{13}(\text{CO})_{24}]$, Albano and co-workers postulated positions for the H atoms based on an analysis of the sizes of the square pyramidal cavities (5, 6). Arguing that H-filled cavities should be slightly larger than empty cavities, they correctly deduced the H positions that we find in the present study (17). Our results also show that the occupied holes are slightly larger [average Rh–Rh = $2.78(1) \text{ \AA}$] than the unoccupied holes [average Rh–Rh = $2.75(1) \text{ \AA}$], here just detectable at the 3σ level (18).

From our results, analogies can be drawn with studies of chemisorbed H on metallic surfaces. The location of the H atoms in the square pyramidal cavities of $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$ resembles the filling of fourfold hollows on a Rh(100) surface. It is generally accepted that these high-coordination sites are the most energetically favorable positions for chemisorbed H atoms on surfaces

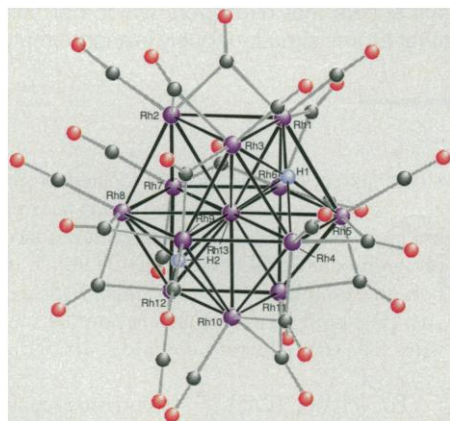


Fig. 1. A view of the $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$ cluster complete with all CO groups. The 13 Rh atoms are arranged in a hexagonal close-packed motif, forming a closed polyhedron that can be described as a truncated trigonal prism, with one additional Rh atom at the center. The cluster is surrounded by 12 terminal CO ligands (one on each surface Rh) and 12 bridging CO groups.

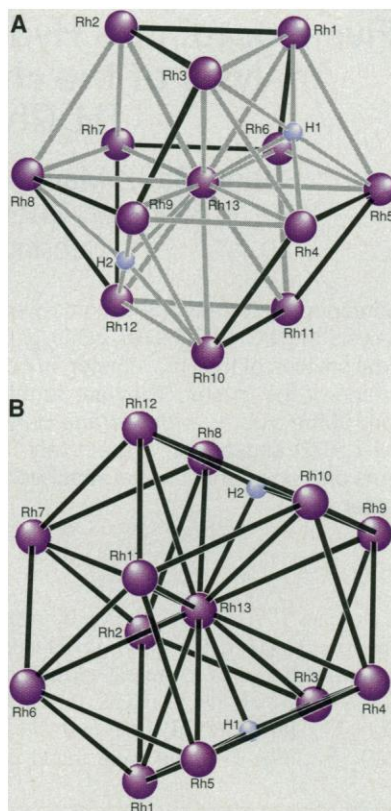


Fig. 2. (A) The H_2Rh_{13} core in $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$, showing the two interstitial H atoms. The black lines represent Rh–Rh bonds bridged by CO ligands, whereas the gray lines indicate Rh–Rh bonds without CO bridges. (B) Alternative view of the H_2Rh_{13} cluster, emphasizing the near coplanarity of the two H atoms with the surface atoms of the cluster. There is a very slight inward displacement of the H atoms toward the central Rh atom.

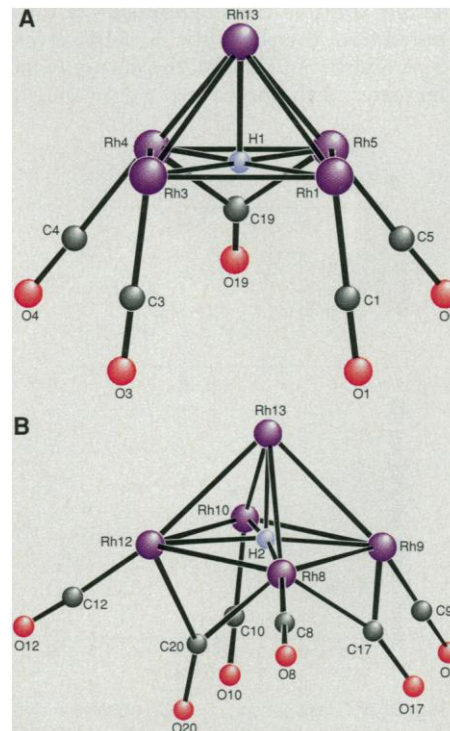


Fig. 3. (A) Plot of the environment around H1, including the CO ligands. This cavity is situated on the noncrystallographic mirror plane of the Rh_{13} cluster and is the only one that has just one bridging CO group. (B) Plot of the environment around H2, including the CO ligands. The ligands in (B) are arranged differently as compared to those in (A). This is one of two cavities in the Rh_{13} cluster that have two bridging CO groups.

of fourfold symmetry (19). Although the detailed geometry of this particular arrangement [H on Rh(100)] has not yet been determined (20, 21) by structural techniques such as low-energy electron diffraction (LEED) or He atom scattering, vibrational studies (from electron energy loss spectroscopy) support the assignment of H atoms in fourfold hollows (22). Theoretical calculations (23) predict that the H atoms are close to being coplanar with the layer of Rh atoms but are displaced by about 0.38 to 0.65 Å above the Rh(100) plane. Our results are consistent with the main features of this conclusion, although we find the displacement of the H atoms to be in the opposite direction. This difference may be due to the fact that in our case we have a carbonyl-covered "surface."

Another parallel can be drawn between our system and solid-state metal hydrides. The H atoms in the $[\text{H}_x\text{Rh}_{13}(\text{CO})_{24}]^{(5-x)-}$ clusters are fluxional, a phenomenon highly reminiscent of the well-known mobility of H atoms in bulk metal hydrides (24). The solution ^1H nuclear magnetic resonance (NMR) spectrum of the title anion shows that the H atoms are mobile (25) on the NMR time scale at room temperature (7,

8). There is evidence that the H atoms do not move onto the surface of the Rh_{13} cluster during this exchange, allowing the conclusion that migration of H atoms must take place in the interior of the cluster itself (7, 8). The mechanism by which the H atoms "hop" from site to site is not resolved yet, although it would seem that the most obvious route is a path through the tetrahedral cavities of the cluster.

The factors that determine whether or not a H atom enters a cavity are not yet fully understood. The presence of an interstitial vacancy does not necessarily mean that a H atom will automatically fill it. For example, a neutron diffraction analysis on $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{2-}$ shows the four H atoms on surface sites (two edge-bridging and two face-bridging), even though an octahedral cavity is vacant and available (26). In $[\text{HCo}_6(\text{CO})_{15}]^-$ the H atom is interstitial (1), but in the isoelectronic compound $[\text{HRh}_6(\text{CO})_{15}]^-$ it is not, preferring instead to be on a surface (terminal μ_1 -H) position (27). The fact that the H atom in $[\text{HRh}_6(\text{CO})_{15}]^-$ is not interstitial is puzzling, because our work clearly shows that there is no a priori reason why H atoms would avoid octahedral Rh_6 or pseudooctahedral Rh_5

cavities. Clearly, additional structural investigations are needed before we can fully appreciate the behavior of H atoms in metal clusters.

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10. Crystallographic details for the x-ray analysis of $[\text{N}(\text{CH}_3)_4]_3[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]$ (methyl ethyl ketone solvate) at -110°C : space group $P2_1/n$ (monoclinic), $a = 16.636(3)$ Å, $b = 18.336(1)$ Å, $c = 20.567(7)$ Å, $\beta = 95.02(2)^\circ$, $V = 6250$ Å³, $Z = 4$, $R(F) = 0.049$, $R(wF) = 0.060$ for 5406 reflections with $I > 4\sigma(I)$ (M. Drabnis, Z. Xie, R. Bau, unpublished data). $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$; $R(wF) = [\sum w|F_o| - |F_c|]^2 / \sum w|F_o|^2]^{1/2}$, I is the intensity, and $\sigma(I)$ is its estimated standard deviation.
11. A black crystal of $[\text{N}(\text{CH}_3)_4]_3[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}] \cdot (\text{CH}_3\text{COC}_2\text{H}_5)$ (volume, 1.8 mm³) was mounted on an Al pin with halocarbon grease and sealed under a He atmosphere inside an Al container at a temperature of 15.0 ± 0.5 K. Intensity data were obtained over one quadrant of reciprocal space, and integrated intensities $\langle I_o \rangle$ and variances $[\sigma^2(I_o)]$ were derived from the scan profiles as described in (12). Lorentz factors were applied, as well as an absorption correction (13). Transmission factors were in the range 0.769 to 0.847. Averaging over 406 symmetry-related pairs of reflections resulted in an internal agreement factor of $R(\text{int}) = 0.094$ and yielded 11,014 total observations. Crystallographic details at 15 K: space group $P2_1/n$ (monoclinic), $a = 16.239(6)$ Å, $b = 17.887(7)$ Å, $c = 20.080(8)$ Å, $\beta = 94.62(3)^\circ$, $V = 5813$ Å³, $Z = 4$.
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14. Because of the extremely small size (by neutron diffraction standards) of the crystal, we found it necessary to collect data very slowly (approximately 150 reflections per day), and the data set was quite weak. Consequently, the agreement factor is somewhat higher than normally expected. Distances and angles quoted in this report are based on the refinement with all data. A complete set of supplementary tables for this structure analysis, including atomic coordinates, interatomic distances and angles, has been deposited with the Cambridge Crystallographic Data Centre (UK) as CADC-100105.
15. *Interatomic Distances Supplement* (Spec. Publ. 18, Chemical Society, London, 1965), p. S10s.
16. Recently we have also noticed a similar trend in analyzing Co-H distances: Co-H = 1.558(18) Å for μ_1 -H, 1.641(6) Å for μ_2 -H, 1.734(4) Å for μ_3 -H, and 1.823(13) Å for μ_6 -H [F. Lutz *et al.*, *Inorg. Chem.* **35**, 2698 (1996)].
17. In the original x-ray work (5, 6), it was predicted that the first H atom would be found in the unique cavity bridged by one CO ligand [Rh(1,3,4,5,13)], and the second H atom in one of the cavities bridged by two CO groups [Rh(8,9,10,12,13)].
18. In our neutron analysis, the eight surface Rh-Rh dis-

Table 1. Selected distances and angles in $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$. (Atomic notation is as in Fig. 1. Standard deviations are in parentheses.)

Distances (angstroms)			
Rh1-H1	1.928(23)	Rh8-H2	1.920(23)
Rh3-H1	1.964(25)	Rh9-H2	1.961(24)
Rh4-H1	2.046(23)	Rh10-H2	1.938(23)
Rh5-H1	2.026(25)	Rh12-H2	2.014(24)
Rh13-H1	1.827(21)	Rh13-H2	1.861(22)
Angles (degrees)			
Rh1-H1-Rh3	93.6(10)	Rh8-H2-Rh9	89.9(10)
Rh1-H1-Rh4	175.9(11)	Rh8-H2-Rh10	173.2(12)
Rh3-H1-Rh4	88.9(10)	Rh8-H2-Rh12	89.5(9)
Rh1-H1-Rh5	91.6(10)	Rh8-H2-Rh13	93.1(10)
Rh3-H1-Rh5	173.7(12)	Rh9-H2-Rh10	92.0(9)
Rh4-H1-Rh5	85.7(9)	Rh9-H2-Rh12	174.0(12)
Rh1-H1-Rh13	92.1(10)	Rh9-H2-Rh13	95.5(10)
Rh3-H1-Rh13	92.2(10)	Rh10-H2-Rh12	87.9(10)
Rh4-H1-Rh13	91.1(9)	Rh10-H2-Rh13	93.3(10)
Rh5-H1-Rh13	91.2(10)	Rh12-H2-Rh13	90.5(10)
H1-Rh13-H2	130.8(11)		

Table 2. Variation of the Rh-H distance with hydrogen coordination number.

Compound*	H coordination number	Rh-H distance (Å)	Reference
$[\text{Rh}_2\text{H}_2(\mu_2\text{-H})_2\text{L}_2]^{2+}$	1	1.536(2)	(28)
$\text{RhH}_2(\text{C}_5\text{Me}_5)(\text{SiEt}_3)_2$	1	1.581(3)	(29)
$[\text{Rh}_2\text{H}_2(\mu_2\text{-H})_2\text{L}_2]^{2+}$	2	1.754(2)	(28)
$\text{Rh}_3(\mu_2\text{-H})_3[\text{P}(\text{OCH}_3)_3]_6$	2	1.765(11)	(30)
$[\text{Rh}_4(\mu_3\text{-H})_4(\text{C}_5\text{Me}_5)_4]^+[\text{BF}_4]^-$	3	1.859(6)	(31)
$[\text{Rh}_{13}(\mu_5\text{-H})_2(\text{CO})_{24}]^{3-}$	5	1.948(21)	This work

*L = 1,4,7-trimethyl-1,4,7-triazacyclononane; Me = methyl; Et = ethyl.

- tances of the two occupied cavities, Rh(1,3,4,5) and Rh(8,9,10,12), average to 2.78(1) Å, whereas the 16 surface Rh-Rh distances of the four unoccupied cavities average to 2.75(1) Å. This represents a 1% expansion in the dimensions of filled holes relative to empty holes and is consistent with (but smaller than) the 2 to 3% expansion deduced from earlier x-ray work (6). Studies on the binary Rh-H system also support an increase in metal-metal distance upon occupation of a cavity by H, with expansions typically in the 5% range [see S. Wilke, D. Hennig, R. Löber, *Phys. Rev. B* **50**, 2548 (1994)].
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 25. The fluxional NMR behavior of $[\text{H}_2\text{Rh}_{13}(\text{CO})_{24}]^{3-}$, however, does not persist at low temperature in solution (-95°C) (8), nor does it occur in the solid state [T. Eguchi *et al.*, *J. Chem. Soc. Dalton Trans.* **1996**, 625 (1996)].
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Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering

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Optical detection and spectroscopy of single molecules and single nanoparticles have been achieved at room temperature with the use of surface-enhanced Raman scattering. Individual silver colloidal nanoparticles were screened from a large heterogeneous population for special size-dependent properties and were then used to amplify the spectroscopic signatures of adsorbed molecules. For single rhodamine 6G molecules adsorbed on the selected nanoparticles, the intrinsic Raman enhancement factors were on the order of 10^{14} to 10^{15} , much larger than the ensemble-averaged values derived from conventional measurements. This enormous enhancement leads to vibrational Raman signals that are more intense and more stable than single-molecule fluorescence.

Recent advances in ultrasensitive instrumentation have allowed the detection, identification, and dynamic study of single molecules in low-temperature solids (1–3), in room-temperature liquids (4, 5), and on dielectric surfaces (6–9). This capability opens many opportunities for scientists in various disciplines such as analytical chemistry, molecular biology, and nanostructured materials (10–12). Current methods for probing single molecules, however, are restricted to a few basic principles. These mainly include laser-induced fluorescence with near-field, far-field, and evanescent-wave excitation, frequency-modulated optical absorption at low temperatures (1, 2), and electrochemical detection of redox-active species (13). We report a methodology based on surface-enhanced Raman scatter-

ing (SERS) (14) for studying single molecules adsorbed on single nanoparticles at room temperature. By coupling single molecules to nanoparticles, we demonstrated that nanometer-sized particles can amplify the spectroscopic signatures of single molecules enormously and that the size-dependent properties of nanostructures can be examined at the single-particle level.

Single-molecule detection by SERS is expected to extend and complement fluorescence studies. Except in low-temperature solids (15), fluorescence measurements do not provide detailed molecular information, and photobleaching often limits the number of photons obtainable from a single molecule. These problems could be overcome with the use of Raman spectroscopy, which is capable of providing highly resolved vibrational information and does not suffer from rapid photobleaching. However, Raman scattering is an extremely inefficient process, and its cross sections ($\sim 10^{-30}$ cm² per molecule) are about 14

orders of magnitude smaller than those of fluorescent dyes ($\sim 10^{-16}$ cm² per molecule). To achieve single-molecule detection sensitivity, the normal efficiency of Raman scattering must be enhanced 10^{14} -fold or more. We demonstrate that such enormous degrees of signal amplification can be obtained by exploiting the surface-enhanced Raman effect and the resonance enhancement effect. Recently, Kneipp *et al.* (16) reported similar magnitudes of surface enhancement and detected single-molecule Raman signals with near-infrared laser excitation.

An unexpected finding during this work was that a very small number of nanoparticles exhibited unusually high enhancement efficiencies. These particles emitted bright, Stokes-shifted (toward longer wavelengths) light and are called "hot particles." To screen for these hot particles in a heterogeneous Ag colloid solution, we incubated an aliquot of the colloid with rhodamine 6G (R6G) molecules for an extended period of time (~ 3 hours) at room temperature. The colloidal particles were immobilized on polysilane-coated glass surfaces because of the electrostatic interactions between the negative charges on the particles and the positive charges on the surface (17). Other methods using organosilane and thiol compounds are also available for immobilizing and dispersing colloidal particles on surfaces (18). Morphological studies by transmission electron microscopy and atomic force microscopy (AFM) showed that the colloid was a mixture of heterogeneous particles with an average particle size of about 35 nm and a typical concentration of $\sim 10^{11}$ particles/ml. With wide-field laser illumination, about 200 to 1000 immobilized particles were examined in one field of view or a $100 \mu\text{m} \times 100 \mu\text{m}$

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