# Reports

## Visibility of Single Atoms

Abstract. *Theoretical and experimental studies indicate that, with a high-resolution scanning electron microscope, it is now possible to obtain pictures of a single heavy atom resting on a thin carbon substrate.*

The attempt to render single atoms visible has been one of the central themes in the development of the electron microscope. Substantial improvements in the resolving power of these instruments has taken place in the last two decades, but it has not been possible to obtain an image of a single, isolated atom.

It is not likely that a conventional electron microscope can be used for such purposes, because, although the resolving power is great enough, the visibility of an atom is far too low—the conventional microscope suffers from a low contrast in the micrograph. An exception to this generalization is the use of darkfield microscopy, and with such a technique it may be possible to see single atoms. However, there is no experimental evidence for such a capability.

A high-resolution scanning microscope has been developed in our laboratory (*1*); this instrument appears to offer some advantages with respect to the contrast although the resolving power (5 Å) is not as great as that of commercial conventional microscopes.

The scanning microscope consists of an electron-optical system which produces a focused spot of electrons about 5 Å in diameter, containing an electron current of $10^{-11}$ to $10^{-10}$ ampere and having a beam convergence angle of approximately 20 milliradians (mr). The specimen is placed at the focus, and the beam can be scanned across the specimen in a square raster.

If a total of $N$ electrons is incident on the specimen, then $N_e$ electrons will be elastically scattered, $N_i$ will be inelastically scattered, and $N_0 = N - N_e - N_i$ will be totally unaffected by the specimen. Theoretical cross-section calculations by Lenz (*2*) can be simplified to give

$$\frac{N_e}{N} = \frac{46.5 \cdot Z^{4/3}}{\sigma_b \cdot V} n = \frac{n\sigma_e}{\sigma_b}$$

$$\frac{N_i}{N} = \frac{868 \cdot Z^{1/3}}{\sigma_b \cdot V} n = \frac{n\sigma_i}{\sigma_b}$$

for a thin specimen where $Z$ is the atomic number, $V$ is the accelerating voltage (in our case $V = 30$ kv), $\sigma_b$ is the cross-sectional area of the electron beam, and $n$ is the number of atoms in the beam; $\sigma_e$ and $\sigma_i$ are the elastic and inelastic scattering cross-sections. (Cross-sections are in Å$^2$.)

The elastic scattering process is characterized by large scattering angles (50 to 100 mr), so that most of these electrons are scattered outside the cone of illumination (20 mr). The inelastic process is such that angles of scattering are small ($\sim 1$ mr), and most electrons stay within the cone of illumination.

An annular-shaped detector can be placed below the specimen such that the outer diameter subtends several hundred milliradians at the specimen, while a hole in the center allows electrons which subtend 20 mr or less to pass through. This detector will then measure predominantly $N_e$.

The electrons that pass through the hole in the detector can be separated into the two components $N_0$ and $N_i$ by means of an energy analyzing spectrometer.

Of particular interest here is the signal $N_e/N_i$ since it can be seen that

$$N_e/N_i \sim Z/19$$

which is independent of specimen thickness or the energy of the electron beam.

We consider a single atom (say uranium) resting on a carbon film 20 Å thick. Such films can be readily made and are not too fragile for use in the microscope.

We can calculate the expected values for $N_e$ and $N_i$ for the carbon (C) film and for the carbon film plus one uranium atom (C + U).

$$\frac{N_e^{U+C}}{N} = \frac{\sigma_e^U + n_C\sigma_e^C}{\sigma_b}$$

$$\frac{N_e^C}{N} = \frac{n_C\sigma_e^C}{\sigma_b}$$

$$\frac{N_i^{U+C}}{N} = \frac{\sigma_i^U + n_C\sigma_i^C}{\sigma_b}$$

$$\frac{N_i^C}{N} = \frac{n_C\sigma_i^C}{\sigma_b}$$

where $n_C$ is the number of carbon atoms in the beam (approximately 55 in our case).

Subscripts e refer to elastic scattering, subscripts i refer to inelastic scattering. The superscripts are self-explanatory.

We now have

$$\frac{N_e^{U+C}}{N_e^C} = 1 + \frac{1}{n_C}\frac{\sigma_e^U}{\sigma_e^C}$$

$$= 1 + \frac{1}{n_C}\left(\frac{92}{6}\right)^{4/3}$$

$$= 1.68$$

We call this number the visibility factor, and it indicates that when the elastically scattered electrons are used alone the signal on uranium plus carbon should be 1.68 times the signal on carbon alone.

We can also calculate the visibility factor when we use the ratio $N_e/N_i$ as the signal in the microscope.

$$\frac{N_e^{U+C}}{N_i^{U+C}} = \frac{\sigma_e^C}{\sigma_i^C}\left[\frac{n_C + (\sigma_e^U/\sigma_e^C)}{n_C + (\sigma_i^U/\sigma_i^C)}\right]$$

$$\sim 1.68\ N_e^C/N_i^C$$

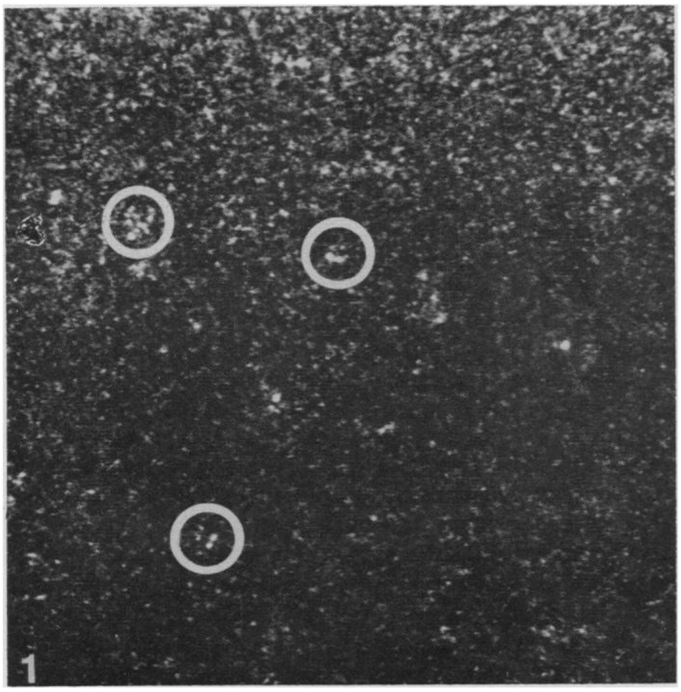
That is, the visibility for the ratio signal should be approximately the same as for the elastic signal above. This indicates that a single uranium atom will be visible if the signals are statistically good enough to allow the separation. There are two principal sources of noise; one of these is the variation in the thickness of the carbon film itself, and the other is the statistical variation of the number of electrons collected.

The assumed number of carbon atoms is 55 so that the statistical variations are of the order of 13 percent. The statistical variations of the various electronic signals can be shown to be smaller than this, and in our normal operating mode these variations should be less than 10 percent. Specifically we assume a beam current of $3 \times 10^{-11}$ ampere, and a 600-line picture is formed in 10 seconds. The number of electrons per picture element is then $5 \times 10^3$. From the cross-sectional data above, the number of elastically scattered electrons from carbon will be approximately 170. At worst we will assume that the picture element corresponds to the resolution element, although to be prudent one would make it a little smaller to avoid the possibility of missing an atom. Combining these two sources of error we would say that the noise should be less than 20 percent, and there should be no problem in seeing a single uranium atom.

When only the elastically scattered electrons are used, we expect that the variations in signal due to the local variations in thickness of the carbon film will be the predominant source of background noise. This should improve, however, when we use the ratio $N_e/N_i$ as the signal because this signal is independent of the thickness of the carbon film.

Noise in the background can be a source of false signals because, with a probable error of 20 percent, we would expect that, on the average, a signal of 1.6 would occur once every 1000 image points; and we have about $10^5$ image points per picture. However, a real signal from a single atom will appear on every picture, while the others will not. In addition, the use of groups of atoms with a known relation to each other reduces the probability of false identification very significantly.

We have tested these calculations with a variety of specimens. Briefly, our method was to construct various molecules containing heavy atoms whose spacing was greater than 5 Å, and then to ensure that the expected geometrical arrangement could be achieved. The visibility factor



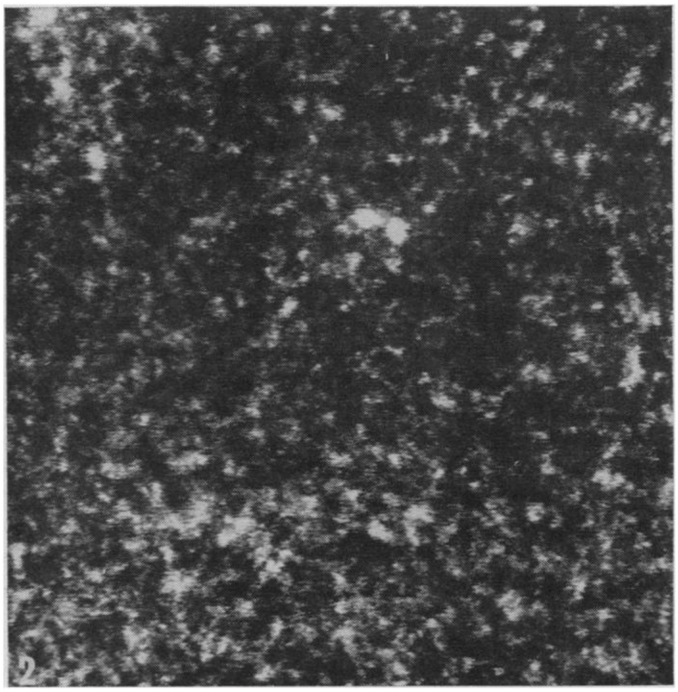
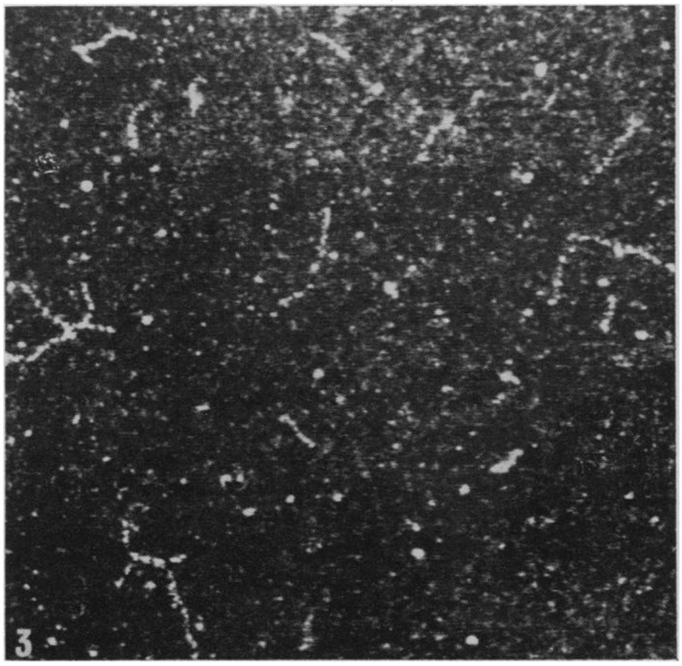


Fig. 1. Micrograph of a thin carbon film which has been coated with a dilute solution of uranyl acetate reacted with benzenetetracarboxylic acid. The expected appearance of the uranium atoms is that they will appear in pairs separated by 13, 23, 33 Å, and so on. This picture was taken using the ratio $N_{\mathrm{e}}/N_{\mathrm{i}}$. Several pairs of bright spots can be seen. These are presumably uranium atoms (2100 Å full scale). Fig. 2. Identical preparation to Fig. 1, except that this micrograph was taken at a higher magnification. A pair of white spots can be seen in the upper center. These are presumably two uranium atoms (670 Å full scale).



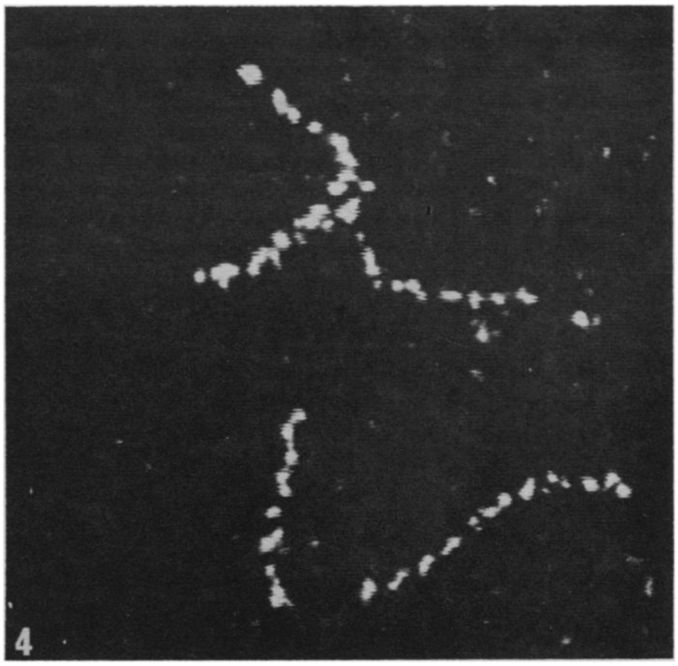


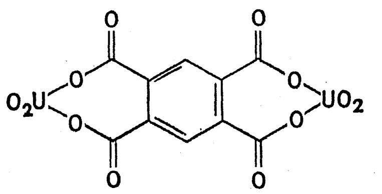
Fig. 3. Micrograph of a thin carbon film which has been coated with a dilute solution of thorium nitrate reacted with benzenetetracarboxylic acid. It was expected that long chains of thorium atoms would be formed separated by 13, 23 Å, and so forth, according to the degree of polymerization of carboxylic acid between thorium atoms. Strings of white spots can clearly be seen, and these are presumably due to the thorium atoms (2100 Å full scale). Fig. 4. Identical preparation to Fig. 3, except that these micrographs were taken at a higher magnification. Although some vibration effects are visible in the micrographs, the separation of the individual atoms can be clearly detected (670 Å full scale).

was then measured by visual observation of the signals from the detectors on an oscilloscope.

*Uranyl acetate.* A dilute solution ($10^{-4}M$) of uranyl acetate was sprayed onto a clean carbon film and allowed to dry. Single bright spots were observed with visibility varying between 1.3 and 1.7. The fact that these were due to material of high Z was verified by taking micrographs with the use of only inelastic electrons. The spots were then invisible, although we observed similar spots which remained bright under these conditions. These may have been due to local concentrations of carbon.

The carbon substrate background noise was not entirely removed by taking the ratio $N_e/N_i$. This is presumably because the inelastic scattering process is not so highly localized as the elastic process.

*Uranium pairs.* At the suggestion of M. Beer, uranyl acetate was reacted with 1, 2, 4,5-benzenetetracarboxylic acid. In this case we expect to produce a molecule



where the two uranium atoms are expected to be separated by about 13 Å.

According to Roberts and Caserio (*3*), carboxylic acids are usually found as dimers in the liquid phase. Because the tetracarboxylic acid is symmetrical, we might expect this particular form to polymerize. In this case, we would expect the spacing of the uranium atoms to be approximately $[13 + (n - 1)10]$ Å, where $n = 2$ for a dimer, and so on.

A dilute solution of the reaction product was sprayed onto clean carbon, and pairs of bright spots were seen (Figs. 1 and 2). These spots have a visibility which varies between 1.4 and 1.7, and the spots disappeared when only the inelastic signal was used. The variation in the spacing is consistent with the idea of polymerization. Spacings attributable to one, two, and three molecules were observed.

*Thorium chains.* Thorium nitrate was reacted with the same carboxylic acid. Thorium is tetravalent and one can therefore make chains of thorium atoms separated by the same organic structure as in the case of uranium. This specimen was made by M. Beer. A dilute solution was sprayed onto clean carbon, and long chains were observed (Figs. 3 and 4). Once again the visibility varied between 1.4 and 1.8, and the spots disappeared when only inelastic electrons were used. Again the average spacing of the spots was somewhat larger than 13 Å, indicating polymerization.

It appears that the bright spots which we have observed are probably due to single atoms. The evidence for this conclusion rests on several facts. (i) The visibility factor is close to the calculated one and is within reasonable error limits. (ii) The spots disappear when we use only inelastic electrons to form an image. (iii) The geometrical arrangement of the bright spots corresponds to the expected one.

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### References and Notes

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4. We thank the many people who made this work possible, with particular gratitude to M. Beer, who provided much needed help and advice on the chemistry involved in the experiments. Supported by AEC.

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## Jupiter's Convection and Its Red Spot

Abstract. *Physical properties of the liquid hydrogen-helium layer of Jupiter are calculated and used in evaluating convection and in interpreting the approximately constant rate of longitudinal motion of the Red Spot on the basis of the Hide-Streett model.*

The Red Spot of Jupiter, known for some 300 years, presents a fascinating object of planetary physics. No satisfactory explanation has been found of its nature and of its huge, remarkably constant rate of longitudinal eastward and westward motion, with an absence of any significant latitudinal motion. Hide's recent proposal (*1*) that what is visible is the top of a Taylor column generated in Jupiter's atmosphere by a surface irregularity has stirred new interest in this problem (*2*). The present report describes an attempt to explain the rate of motion of the spot (about 25 deg/year or $10^2$ cm $\text{sec}^{-1}$) in terms of cellular convection in the liquid region of the planet. The model (*3*) of Jupiter used in these studies is a modification of earlier models and is based on a theoretical analysis of the hydrogen-helium system. It suggests that besides a liquid metallic hydrogen-helium core (which in analogy to Earth probably is the source of the huge magnetic field of the planet) there is a solid metallic hydrogen mantle surrounded by a solid molecular hydrogen-helium mantle and a supercritical atmosphere. The latter, made chiefly of hydrogen, may contain much helium in its lower strata.

If the Taylor column of the Red Spot were associated with an irregularity floating on a liquid surface, then its motion could be the result of convection within the liquid layer. An analysis of this motion is difficult because of the absence of a sufficiently general theory of equatorial convection in a rapidly rotating spherical shell. For instance, the problem of convection (governed by the Rayleigh number $R = g\, \alpha\, \rho^2\, C_p d^4\, \lambda^{-1}\, \eta^{-1}$ grad $T$, where $g$ is gravitational acceleration; $\lambda$, thermal conductivity; $\eta$, viscosity; $d$, thickness of the convecting layer; $\rho$, density; $\alpha$, thermal expansion; $C_p$, specific heat; and grad $T$, the average vertical temperature gradient) has been solved numerically by Durney (*4*), but only for low Rayleigh numbers (about 1500) and low angular velocities not applicable in our case. Certain conclusions can also be drawn from studies of rotating fluid spheres (*5, 6*) rather than shells, but here again the analogies cannot be pushed very far. Finally, much theoretical effort has been directed at analyzing the effect of rotation on convection in the experimentally accessible case when the angular velocity is parallel to the gravitational acceleration. These results are, unfortunately, of little use for the motion of the Red Spot which is so close to the planet's equator. One is forced, therefore, to make assumptions, in particular with respect to the stabilizing effect of rotation on convection. It is well known (*5, 6*) that for low angular velocity the critical Rayleigh number $R_c$, at which convection sets in, is constant but it increases as $Ta^{2/3}$ for $Ta$