

Lawrence Berkeley National Laboratory

LBL Publications

Title

A Diffuse LEED Study of the Adsorption Structure of Disordered Benzene on Pt(111)

Permalink

<https://escholarship.org/uc/item/6rj7h8dv>

Authors

Wander, A.
Held, G.
Hwang, R.Q.
et al.

Publication Date

1991

Center for Advanced Materials

CAM

Submitted to Surface Science

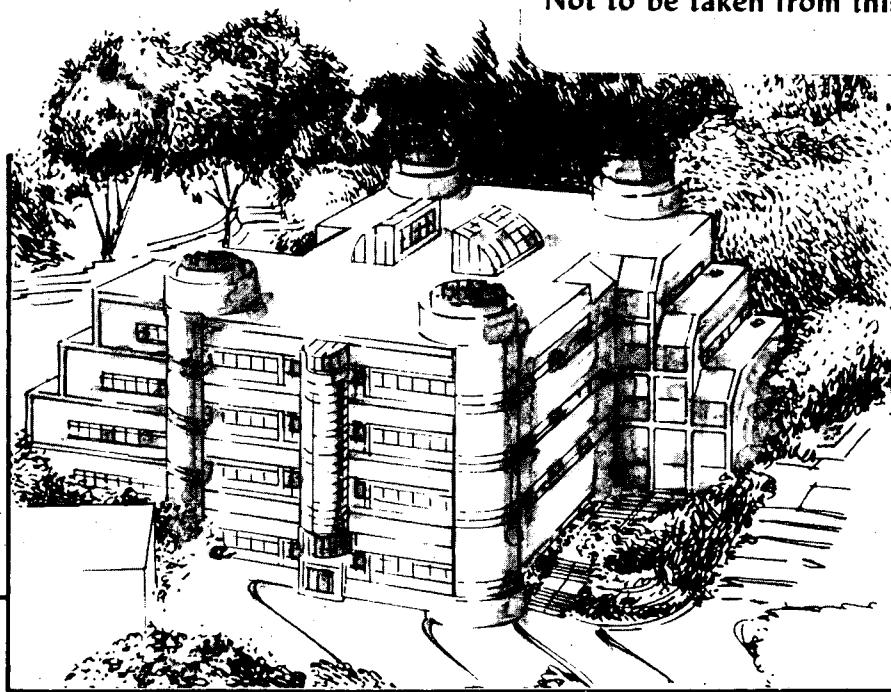
A Diffuse LEED Study of the Adsorption Structure of Disordered Benzene on Pt(111)

A. Wander, G. Held, R.Q. Hwang, G.S. Blackman, M.L. Xu,
P. de Andres, M.A. Van Hove, and G.A. Somorjai

January 1991

For Reference

Not to be taken from this room



Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California
ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

Bldg. 50 Library.

Copy 1

LBL-29475

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

**A Diffuse LEED Study of the Adsorption Structure of Disordered
Benzene on Pt(111)**

A. Wander, G. Held¹, R. Q. Hwang², G. S. Blackman³,
M. L. Xu⁴, P. de Andres⁵,
M. A. Van Hove and G. A. Somorjai.

Materials Science Division
Center for Advanced Materials
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720 U.S.A.

and

Department of Chemistry,
University of California,
Berkeley, CA 94720.

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division, U.S. Department of Energy under contract No. DE-AC03--76SF00098.

¹ Permanent address: Institut für Festkörperphysik, Physik-Dept. E20, Technische Universität München, D-8046 Garching b. München, Fed. Rep. of Germany.

² Permanent address: Institut für Kristallographie und Mineralogie, Theresienstraße 41, Universität München, D-8000 München 2, Fed. Rep. of Germany.

³ Permanent address: IBM Almaden Research Laboratory, K33 281, 650 Harry Road, San Jose, CA 95120-6099, USA.

⁴ Permanent address: Lash Miller Chemistry Laboratories, University of Toronto, 80 St. George St., Toronto, Ontario M5A 1A1, Canada.

⁵ Permanent address: Instituto de Materiales (CSIC) and Departamento de Materia Condensada (UAM), c/Serrano 144, E-28006 Madrid, Spain.

Abstract

Previous LEED structural studies of benzene chemisorption on transition metal surfaces have relied on the presence of coadsorbed carbon monoxide to induce ordering in the overlayer. To investigate the effect of CO on the benzene structure, the disordered pure benzene layer chemisorbed on Pt(111) is studied by diffuse LEED intensity analysis. The diffuse LEED intensity has been measured using a digital LEED apparatus and analysed using an extension of the beam set neglect method. The benzene is found to chemisorb in a two fold bridge site rotated by 30° with respect to the site found for the ordered phase formed in the presence of coadsorbed CO. In addition, the benzene ring is found to be distorted. Parallel distortions are subject to large error bars, but perpendicular spacings have been more accurately determined. These include a buckling distortion not previously seen for benzene chemisorption on transition metal surfaces.

1. Introduction

The bonding of aromatic hydrocarbons to transition metal surfaces plays a crucial role in many catalytic processes. Considerable work has been performed using benzene on platinum single crystals as a model catalytic system. Structural information on this system has been obtained by High resolution electron energy loss spectroscopy (HREELS) [1], low-energy electron diffraction (LEED) [2,3] angle-resolved ultraviolet photoemission spectroscopy (ARUPS) [4] and near-edge x-ray absorption fine structure (NEXAFS) [5]. Previous LEED studies have been limited to ordered overlayers [3]. Pure benzene does not order on Pt(111) at the temperatures considered. Therefore, coadsorption with CO has proved invaluable since it induces ordering on this, and other transition metal, surfaces [3,6-8]. However, it is not known to what extent CO influences the structure of the benzene ring observed in these studies. For example, large distortions of the benzene ring were observed in the coadsorption studies on both Pt(111) and Rh(111). Knowing the structure of pure benzene on Pt(111) should therefore provide insight into both the benzene-Pt interaction and the effects of CO coadsorption.

This paper reports on a structural study of disordered benzene on Pt(111) using diffuse LEED measurement and analysis. New theoretical techniques have recently been developed which allow diffuse LEED intensities created by lattice gas disorder to be analysed [9]. The structure of several disordered systems has been determined using these techniques [e.g. 10,11]. To this point however, only

atomic or small molecular adsorbates have been considered due to limitations of computational time. In this study an extension of the beam set neglect approach used in ordered LEED studies has been used to reduce computational requirements as much as possible. This scheme has previously been applied to disordered CO on Pt(111) [10].

2. Experimental

Experiments were performed in a standard UHV system equipped with a PHI cylindrical mirror analyzer for AES, a UTI quadrupole mass spectrometer, and an ion sputter gun. The base pressure was less than 1×10^{-10} torr. The sample was mounted on a high precision manipulator allowing x, y, and z translations, tilt and azimuthal adjustments. The diffuse LEED measurements were made using a unique digital LEED instrument with a wedge and strip anode detector allowing spatially resolved pulse counting of the diffracted electrons. A complete description of this instrument will be presented in reference [12]. All LEED measurements were performed at normal incidence within a tolerance of $\pm 0.5^\circ$. Spectroscopic grade benzene was purified with many freeze thaw cycles and admitted to the chamber via a Varian leak valve. For maximum scattering intensity high coverage of benzene is desirable. Adsorbate-adsorbate multiple scattering contributions should be small, due to both the low probability of 90° scattering paths and due to the fact that the hydrogen atoms around the benzene ring help to ensure that a layer of planar benzene molecules will be physically well separated. However, care must be exercised in order to prevent

the formation of a multi-layer structure. Lehwald et al have reported EELS evidence of multi-layer growth of benzene on Pt at temperatures below 150K and exposures greater than 5L [1].

Benzene was deposited at a range of pressures from 1×10^{-8} torr to 1×10^{-7} torr. Adsorption was found to saturate at $\approx 2\text{L}$ for substrate temperatures between 170K and 300K. At this coverage, the ratio of the C(272eV) AES peak-to peak height to that of the Pt(237eV) signal was in the range of $C_{272}/Pt_{237} \approx 1.7 - 2.0$. Ogletree et al have solved the ordered structure of CO coadsorbed with benzene to form a $(2\sqrt{3} \times 4)\text{rect}$ overlayer using LEED-IV analysis [3]. This structure implies a C to Pt ratio of about 1. Stair has measured the coverage of this structure with AES and found $C_{272}/Pt_{237} \approx 2.46$ [13]. Therefore, at saturation, a monolayer or less of benzene was formed under our deposition conditions.

An experimental complication is the ordering of benzene due to residual CO. As mentioned above, it is known that benzene orders in a $(2\sqrt{3} \times 4)\text{rect}$ pattern with 0.1L of coadsorbed CO. A crude analysis of the residual background gases gave an estimate of the CO partial pressure of about 2×10^{-11} torr, which would imply a time period of 83 minutes for an exposure of 0.1L. However, the CO partial pressure could increase during deposition due to desorption of CO from the chamber walls and pumps. After 10L deposition of benzene, thermal desorption showed no measurable amount of CO. The LEED pattern of the saturation coverage of benzene at 170K was then monitored at 5 minute intervals for 1 hour.

No indication of ordering was observed. Thermal desorption, however, did show trace amounts of CO. To minimize CO adsorption a recipe following Ogletree was used [14]. The sample was flashed to 1250K and benzene exposure began as soon as the sample temperature dropped below 350K. All measurements were then made within 15 minutes.

All diffuse LEED data were taken at saturation coverage (5L exposure). At each energy, two LEED images were stored; one for the clean surface and one after benzene deposition. Ibach et al have shown that the phonon contributions of the substrate can be effectively cancelled by subtracting the LEED image of the clean substrate from that of the adsorbate covered surface, leaving the diffuse intensity due to the surface structure [15]. Two sets of images were taken at energies 4eV apart in order to construct the logarithmic derivative and hence the Y-function: this operation removes undesirable effects due to long-range correlation within the lattice-gas layer [9,10]. This was done at a series of seven energies for comparison with the calculations.

Experimental Y-functions constructed at 83eV and 134eV were used in the structural analysis. These were chosen for the comparatively large amount of structure contained in the diffuse intensity and their relatively large energy separation. Figure 1 shows raw intensities for the clean and the benzene covered surface at 81eV and 85eV. All images were taken at a sample temperature of 170K. Data in each case were collected for 300 seconds with an average collection rate of 9kHz over the entire screen. Dark count rates just prior to data collection

were less than 40Hz. The peak intensities at the Bragg positions were approximately 5000 times larger than the average diffuse intensity in the images from the clean surface. The increased diffuse intensity due to the benzene overlayer can be clearly seen. In figure 2, the clean surface patterns have been subtracted out and the Bragg spots have been removed. At the lower energies, features consistent with the three fold symmetry of the surface are clearly apparent. For comparison with theory, the experimental Y-functions are scaled down from an initial grid size of approximately 150x150 pixels to an 11x11 grid. This leads to a significant enhancement of the signal-to-noise ratio. These Y-functions are shown in figure 3.

3. Theoretical

A multiple scattering theory of diffuse LEED should calculate the probability that an electron scatters at least once from an adsorbate displaying lattice-gas disorder. Two approaches have been used to calculate the resultant diffuse intensities for a given local geometry.

The first method is the so called 'three step method' of Heinz et al [11]. In this approach the calculation is divided into three stages. Firstly, the incident electron is propagated until its first encounter with an adsorbate, this step is like a standard LEED calculation for a clean surface. Then, all scattering paths which begin and end on an adsorbate are calculated (a NEXAFS like calculation), and finally, the electrons are propagated from their final encounter with the adsorbate into the vacuum, this step is merely a time reversed LEED

calculation. The middle step is of at least third order in multiple scattering, and hence its contribution is generally weak. On the other hand, it is relatively time consuming to compute since it is evaluated in a spherical wave representation.

The second approach, and the one we favor, is an extension of the beam set neglect approach previously applied to ordered LEED calculations for systems with large unit cells [16]. This approach effectively neglects the weak and time-consuming second step of the three step method. The first and third steps are then efficiently combined and computed in a plane wave representation in a method analogous to a standard ordered LEED calculation. The calculation is restricted to the integer order beam set generated by the ordered substrate and a fractional order beam set containing the exit direction and all shifted copies of it generated by the addition of a member of the integer order beam set. The overlayer scattering matrix is then calculated allowing full intra-molecular multiple scattering, but neglecting inter-molecular scattering paths. As a result, only 3rd and higher order multiple scattering events are neglected. These two calculation schemes have previously been tested against each other and shown to produce virtually identical results [9].

In the present calculations, the lines joining the (00) and (10), and (00) and (01) spots have been divided into ten equal segments giving us an 11x11 grid of exit directions on which the calculation is performed. As in the experimental data collection, the diffuse intensities are calculated at two energies spaced 4eV apart to allow construction of the Y-function which is then compared with the

experimental Y-function using the Pendry R-factor as a measure of the goodness of fit between the two data sets.

A further complication is caused by the inner potential. In conventional LEED this can be determined by fitting the theoretical and experimental curves by rigidly shifting the calculated IV curves with respect to the energy axis. In the case of angular-dependent intensities at fixed energies, we have to use a different approach. The value is first estimated by adjusting the value found for the clean surface by the work function change on adsorption of benzene [14]. This value is then refined by performing theoretical calculations at various values of V_0 and comparing them to the experimental data. This second fitting yields virtually no change in the optimum value of $14 \pm 1 \text{ eV}$ which was then used throughout the theoretical calculations.

It is well known that hydrogen is a weak scatterer of electrons. Hence, its contribution to the LEED pattern is only significant at low energies below 20 eV. Because of this, we follow previous studies and treat the benzene molecule as a ring of six carbon atoms and neglect the presence of the hydrogen atoms. This has previously been shown to be a good approximation when dealing with hydrocarbon molecules (e.g. [6]).

For ordered structures, we find that structural error bars are commonly quoted in the literature which empirically correspond to a 20% increase of the R-factor from its minimum value. These error bars are based more on experience than on statistics, as they often include such effects as reproducibility, which are

difficult to quantify. With diffuse LEED, little experience is available to guide our choice of error bars. Therefore we choose to follow the above empirical estimate corresponding to a 20% increase in R-factor value.

4. Structural Analysis

The theoretical data at 134eV were found to be very insensitive to variations of the benzene geometry. Because of this, the data at this energy were only used to perform the initial search through the high symmetry adsorption sites. The data taken at 83eV were found to be much more sensitive to small displacements within the carbon ring, and hence these data were used to investigate the possible presence of distortions of the benzene ring.

The theoretical search through the structural phase space proceeded as follows. Firstly, all high symmetry sites on the surface were investigated assuming an undistorted benzene ring, but allowing the ring radius to vary between 1.30 and 1.60Å in steps of 0.05Å and the benzene to surface distance to vary between 2.00 and 2.55Å in steps of 0.05Å. This led to the identification of the sites labelled $C_{2v}(X \rightarrow Y)$, $C_{2v}(X \rightarrow X)$ and $C_{3v}(\sigma_v)(fcc)$ as the most likely candidate sites. Figure 4 explains the site labels while table 1 summarizes the results of this initial search. As can be seen, the R-factors for these sites are already relatively good at 0.17, 0.30 and 0.28 respectively. The 134eV data confirm this site assignment, but at a much lower level of confidence due to higher R-factors and insensitivity to both perpendicular and parallel displacements of the carbon atoms. The R-factor for the 134eV data was 0.41 for the $C_{2v}(X \rightarrow Y)$ with

variations of the ring radius only raising this to 0.46 for a 0.05Å displacement.

Next, distortions of the benzene ring consistent with the local symmetry of the adsorption site were tried, including both planar and out of plane (buckling) distortions. This was done for the three candidate sites generated from the first part of the structural search at 83eV, leading to about 3,000 different trial structures. Figure 5 explains the labels used to describe these distortions. The search ranges and results of this search are displayed in table 2. As can be seen, distortions have a dramatic effect on the R-factors, lowering the $C_{2v}(X \rightarrow Y)$ site R-factor from 0.17 to about 0.05, the $C_{2v}(X \rightarrow X)$ from 0.30 to 0.08 and the $C_{3v}(\sigma_v)(fcc)$ site value from 0.28 to about 0.09. Figure 6 displays the best theoretical Y-functions for these three structures. While the three structures all have very good R-factors, we follow the empirical described above and assign error bars of about 20% on the R-factor values. Hence, the $C_{2v}(X \rightarrow Y)$ bridge site is clearly the optimum structure found in this analysis. However, it should be noted that in typical LEED studies, symmetry equivalent sections of the experimental data often differ by R-factors of about 0.1 and consequently error bars should be of this order. However, due to the sensitivity and low noise of our digital LEED apparatus, the R-factor between symmetry equivalent sectors of the unit mesh is below 0.04. Consequently, we can, with some certainty, assign our structure as being the optimum structure.

As expected from ordered LEED studies, the sensitivities to displacements parallel to and perpendicular to the surface are very different, due to the choice

of normal incidence. The perpendicular distance can be optimised to approximately $\pm 0.02\text{\AA}$. On the other hand, the internal structure of the benzene ring is less certain. Ring radii can only be optimised to approximately $\pm 0.1\text{\AA}$. The best fit structure for the bridge site is displayed in figure 7.

Finally, as in a previous study [10], site mixing has been tried. This is achieved by the incoherent addition of the intensities from the desired sites scaled with respect to site occupancy. While this is only strictly justified when the long range structure factors of the two sites are the same [17], at low coverage the deviation from this condition should be small, making this an acceptable approximation. While some of the over 600,000 tested combinations give R-factors comparable to the best single site R-factor, no combination produces a result significantly below this value.

5. Results and Discussion

It is clear that our structural analysis is incomplete: there are many more structural parameters that could have been varied, including substrate relaxations, which may be important. Such a search is out of the question with our present theoretical approach. A search using tensor LEED coupled with an automated R-factor minimization scheme would have to be applied, as recently developed for ordered structures [18], but is not yet available for diffuse LEED. Tensor LEED has been applied to a disordered structure before [19], but without an automated search scheme which is essential when many unknown parameters must be determined. Since the best R-factor achieved in this study

is quite small, we feel that effects like substrate relaxations cannot be major in this instance.

Our structure for disordered pure benzene on Pt(111) should be compared with our earlier result for benzene coadsorbed with CO on the same surface in an ordered array [3]. The primary difference is a rotation of the molecule by 30° about the surface normal, while keeping its center above the bridge site. This changes the bonding to the Pt atoms in a significant manner. In the coadsorbed case, all six C atoms of the benzene ring had similar bond lengths to their Pt bonding partners ($2.25 \pm 0.05 \text{ \AA}$), and the planar (non-buckled) arrangement found then was therefore reasonable.

In the pure benzene overlayer, the two apical C atoms (at positions $\vec{r}_1$ in fig. 5b, shown gray in fig. 7) are found to lie almost directly over Pt atoms, yielding short Pt-C bonds of $2.02 \pm 0.02 \text{ \AA}$. The four non-apical C atoms have a very different position relative to the Pt atoms. They appear to be bent away from the surface, giving long Pt-C distances of about $2.58 \pm 0.02 \text{ \AA}$ and $2.61 \pm 0.02 \text{ \AA}$. For comparison, the Pt-C distance obtained from adding covalent radii (assuming a single-bond radius of $0.77 \text{ \AA}$ for C) is $2.16 \text{ \AA}$; this distance would decrease if we assumed an (unlikely) multiple bond between Pt and C. Methylacetylene on Rh(111) provides similar bond lengths [20]. The two carbons forming the triple bond within gas-phase methylacetylene bond in almost the same way to Rh(111) as do the non-apical carbon pairs of benzene on Pt(111). They have bonds of length $1.95 \pm 0.1 \text{ \AA}$ to two separate metal atoms, and bonds

of length $2.43 \pm 0.1 \text{ \AA}$ to a common metal atom (the Rh metallic radius is about $0.05 \text{ \AA}$ smaller than that of Pt).

Another relevant comparison is the Pt-C bond in CO adsorption on Pt(111) [10], namely $2.08 \pm 0.07 \text{ \AA}$ in the bridge site and $1.85 \pm 0.10 \text{ \AA}$ in the top site. And the Pt-C bond length for ethynidyne adsorbed in a hollow site on Pt(111) is $2.00 \pm 0.04 \text{ \AA}$ [21]. Furthermore, Pt-C distances for chemisorbed carbon atoms on Pt(111) are $2.03 \pm 0.07 \text{ \AA}$ [22]. These numbers seem to imply relatively strong bonds between Pt and the two apical C atoms, but very weak bonds to the other four C atoms. One might wonder whether the benzene could tilt to shorten one half of those long bonds; since the HREELS data show no clear evidence of tilting [1], this geometry was considered unlikely and was not explored in our search.

The C-C distances which we find within the benzene molecules indicate significant distortions. The two apical C atoms have bonds of length $1.45 \pm 0.10 \text{ \AA}$ to their C neighbors; the bond lengths between these four non-apical C atoms are $1.63 \pm 0.05 \text{ \AA}$, the gas-phase benzene value being $1.397 \text{ \AA}$. This contrasts with an earlier NEXAFS study which found equal bond lengths of $1.40 \pm 0.02 \text{ \AA}$ [9]. An ARUPS investigation concluded on the other hand that a $C_{3v}(\sigma_d)$ Kekulé distortion exists in this system [8]. For comparison, the C-C single, double and triple bond lengths are 1.54 , 1.33 and $1.20 \text{ \AA}$, resp. Thus we find both a significant expansion and a definite symmetry breaking in accord with the site symmetry. In addition the non-apical C atoms move out of the benzene plane

away from the surface by about $0.16\text{\AA}$. This corresponds to a 7° upward tilt of the plans that include the apical C atoms and a pair of non-apical C atoms. In the ordered coadsorbed structure on Pt(111), the C-C bonds were larger: $1.65\pm 0.15\text{\AA}$ and $1.76\pm 0.15\text{\AA}$. However, no out-of-plane bending was found in the coadsorbed structure.

Thus, our data indicate that the effect of CO coadsorption on Pt(111) is a rotation of benzene, with associated changes in Pt-C distances and smaller distortions. Coadsorption is known to be capable of such effects. For instance, coadsorbing CO and benzene on Rh(111) changes the adsorption site of benzene from bridge to hollow [6,7]. And conversely, benzene changes the adsorption site of CO towards higher coordination on Rh(111), although apparently not on Pt(111) (the CO site assignment when coadsorbed with benzene on Pt(111) is uncertain though [3]) and not on Pd(111) [8]. Also the C-O bond elongates upon coadsorption with hydrocarbons [3,6-8].

Two theoretical total-energy calculations have investigated the adsorption of benzene on Pt(111), using the atom superposition and electron delocalisation theory [23] and extended Hückel theory [24]. Both favor either 3-fold hollow sites or 2-fold bridge sites, the preference depending on cluster size, etc. The favored bridge site geometry, however, has the $C_{2v}(X\rightarrow X)$ orientation, i.e. the benzene rotated 30° from our DLEED result.

We may also compare the present benzene structure with our earlier structures on Rh(111) and Pd(111), which were ordered due to CO coadsorption

[6-8]. On both those surfaces, the benzene molecules were found centered on hollow sites (fcc hollow on Pd, hcp hollow on Rh). On Pd(111), we could not detect unequivocally any C₆ ring distortion from the gas-phase geometry, within the error bars of 0.1 Å. On Rh(111), however, a strong Kekulé distortion was apparent, with short/long C-C bonds of 1.46/1.58 Å for a 1:2 mix of benzene:CO, and 1.33/1.81 Å for a 1:1 mix (with error bars of 0.15 Å). Of interest also are the metal-C bond lengths: 2.39 Å on Pd, and 2.30 and 2.35 Å on Rh for the two mix ratios, respectively (with error bars of 0.05 Å). These are intermediate between the short and the long Pt-C bond lengths found in this study.

The C-C distances can also be compared with similar values found in other molecules adsorbed on transition metal surfaces, in particular with small straight-chain hydrocarbons that adsorb parallel to several close-packed metal surfaces. These bond in a way quite similar to the non-apical C-C pairs in benzene on Pt(111). This bonding, with the C-C pair centered approximately over a hollow site, is often referred to as di- σ/π . In acetylene [25], methylacetylene [20] and ethylene [26], one typically finds expansions from the gas-phase bond lengths of 1.20 and 1.33 Å, resp., to 1.45-1.55 Å. Thus in benzene on Pt(111) comparable values of 1.45 ± 0.10 Å and 1.62 ± 0.05 Å are found.

Several organometallic complexes include a benzene ligand bonded to two or three metal atoms. They generally exhibit a C₆ ring expansion, as well as distortions that break the six-fold gas-phase symmetry of benzene according to the symmetry of the metal atom positions. Two complexes with two metal

atoms are $(\text{CpVH})_2(\text{C}_6\text{H}_6)$ [27] and $(\text{PdAl}_2\text{Cl}_7\text{C}_6\text{H}_6)_2$ [28]. They provide a metal symmetry like that of the bridge site on Pt(111), although two more metal atoms are involved in the surface case. One complex has V-C distances of 2.15-2.17 Å and of 2.56-2.58 Å, and C-C distances of 1.42-1.44 Å. The other complex has Pd-C distances of 2.26-2.31 Å and of 2.54-2.63 Å, and C-C distances of 1.36-1.49 Å. Some bending of the benzene plane is also observed in these cases.

Complexes in which benzene ligands bond to 3 metal atoms include $\text{Ru}_6\text{-C}(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ ($\eta^6\text{-C}_6\text{H}_6$) and $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ [29]. In the first complex, the Ru-C bond lengths range from 2.21 to 2.35 Å, while the C-C bonds range from 1.37 to 1.50 Å. In the second complex, the corresponding ranges are 2.27-2.42 Å for Os-C bonds and 1.37-1.56 Å for C-C bonds.

Thus we see benzene deformations on the Pt(111) surface that match qualitatively those found in organometallic complexes. The distortions tend to be larger on the extended surface, probably because more metal atoms influence each benzene. There is however no apparent relationship that would indicate where long and short metal-C and C-C bonds occur, even within the cluster examples. It is also difficult to distinguish between the coadsorbed and non-coadsorbed cases in clusters, because the abovementioned clusters all include coadsorbates, i.e. other ligands.

Acknowledgements:

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and in part by the Army Research Office. Supercomputer time in different stages of the analysis was provided by the Office of Energy Research of the U.S. Department of Energy and by the University of California at Berkeley. AW acknowledges support from NATO via the SERC UK, GH from the Technische Universität München and PdA from NATO.

References

1. S. Lehwald, H. Ibach, and J.E. Demuth, *Surface Sci.* **78** (1978) 577.
2. H. Ohtani, M.A. Van Hove and G.A. Somorjai, in "*The Structure of Surfaces II*", Eds. J.F. van der Veen and M.A. Van Hove, Springer-Verlag (Heidelberg) (1988), p. 219.
3. D.F. Ogletree, M.A. Van Hove and G.A. Somorjai, *Surface Sci.* **183** (1987) 1.
4. J. Somers, M.E. Bridge, D.R. Lloyd and T. McCabe, *Surface Sci.* **181** (1987) L167.
5. J.A. Horsley, J. Stöhr, A.P. Hitchcock, D.C. Newbury, A.L. Johnson and F. Sette, *J. Chem. Phys.* **83** (1985) 6099.
6. M.A. Van Hove, R.F. Lin and G.A. Somorjai, *J. Am. Chem. Soc.* **108** (1986) 2532.
7. R. F. Lin, G.S. Blackman, M.A. Van Hove and G.A. Somorjai, *Acta Crys.* **B43** (1987) 368.
8. H. Ohtani, M.A. Van Hove and G.A. Somorjai, *J. Phys. Chem.* **92** (1988) 3974.
9. D.K. Saldin, J.B. Pendry, M.A. Van Hove and G.A. Somorjai, *Phys. Rev.* **B31** (1985) 1216.

10. G.S. Blackman, M.L. Xu, D.F. Ogletree, M.A. Van Hove and G.A. Somorjai, *Phys. Rev. Lett.* **61** (1988) 2352.
11. K. Heinz, D.K. Saldin, J.B. Pendry, *Phys. Rev. Lett.* **55** (1985) 2312.
12. D.F. Ogletree, G.S. Blackman, R.Q. Hwang, J.E. Katz and G.A. Somorjai, *in preparation*.
13. P.C. Stair and G.A. Somorjai, *J. Chem. Phys.* **67** (1977) 4361.
14. D.F. Ogletree, PhD thesis, University of California, Berkeley 1986.
15. H. Ibach, S. Lehwald, *Surface Sci* **176** (1986) 629.
16. M.A. Van Hove in "*Chemistry and Physics of Solid Surfaces VII*", Eds. R.F. Howe and R. Vanselow, Springer-Verlag (Heidelberg) (1988), p.513.
17. J. C. Le Bossé, J. Lopez, J. Rousseau, I. Zasada, L. Wojtczak, *in preparation*.
18. P.J. Rous, M.A. Van Hove and G.A. Somorjai, *Surf. Sci.* **226** (1990) 15.
19. P.J. Rous, J.B. Pendry, D.K. Saldin, K. Heinz, K. Müller and N. Bickel, *Phys. Rev. Lett.* **57** (1986) 2951.
20. M.A. Van Hove, C.M. Chan, G. Casalone, R.J. Koestner and G.A. Somorjai, *in preparation*.

21. L.L. Kesmodel, L.H. Dubois and G.A. Somorjai, *J. Chem. Phys.* **70** (1979) 2180.
22. Z.P. Hu, D.F. Ogletree, M.A. Van Hove and G.A. Somorjai, *Surface Sci.* **180** (1987) 433.
23. A.B. Anderson, M.R. McDevitt and F.L. Urbach *Surface Sci.* **146** (1985) 80.
24. C. Minot, M.A. Van Hove and G.A. Somorjai, *in preparation*.
25. J. Stöhr, F. Sette and A.L. Johnson, *Phys. Rev. Lett.* **53** (1984) 1684.
26. J.A. Horsley, J. Stöhr and R.J. Koestner, *J. Chem. Phys.* **83** (1985) 3146.
27. V. Wismer, Ph.D. Thesis, Bochum Univ. (Germany), 1981.
28. G. Nardin, P. Delise and G. Allegra, *Gazz. Chim. Ital.* **105** (1975) 1047.
29. M.P. Gomez-Sal, B.F.G. Johnson, J. Lewis, P.R. Raithby and A.H. Wright, *J. Chem. Soc., Chem. Commun.* 1985, 1682.

Figure Captions

Figure 1: Raw intensity data at normal incidence for (a) the clean and (b) benzene covered surface at (i) 81eV and (ii) 85eV. Brightness is proportional to intensity.

Figure 2: The intensity data of fig. 1 after subtraction of the clean surface contribution and suppression of the Bragg spots. Labels as per figure 1.

Figure 3: Experimental Y-functions at (a) 83eV (based on 81eV and 85eV data) and (b) 134eV (based on 132eV and 136eV data).

Figure 4: High symmetry sites for benzene on the Pt(111) surface.

Figure 5: Explanation of the labels used to describe the distortions of the benzene ring tried during the structural search. The origin for vectors $\vec{r}_{1,2}$ lies $d_{\perp}$ above the topmost plane of the platinum atoms. The vectors $\vec{r}_1$ are parallel to the surface, θ is the angle between vector $\vec{r}_2$ and the plane parallel to the surface containing vectors $\vec{r}_1$. The angle β describes lateral angular distortions:

$$(a): \text{3-fold symmetry,} \quad \angle \vec{r}_1 | \vec{r}_2 = 60^\circ - \beta$$

$$\angle \vec{r}_2 | \vec{r}_1 = 60^\circ + \beta$$

$$(b): \text{2-fold symmetry,} \quad \angle \vec{r}_1 | \vec{r}_2 = \angle \vec{r}_2 | \vec{r}_1 = 60^\circ - \beta$$

$$\angle \vec{r}_2 | \vec{r}_2 = 60^\circ + 2\beta$$

Figure 6: The best fit theoretical Y-functions for the bridge-sites (a) $C_{2v}(X \rightarrow Y)$

and (b) $C_{2v}(X \rightarrow X)$ and (c) the hollow site $C_{3v}(\sigma_v)(fcc)$, at 83eV. These should be compared with the experimental plots shown in figure 3.

Figure 7: The best fit structure: $C_{2v}(X \rightarrow Y)$ site with radii $r_1=1.45\text{\AA}$, $r_2=1.55\text{\AA}$ and distortion angles $\theta = +6^\circ$, $\beta = 2^\circ$.

Top: Cross section along the $[1\bar{2}1]$ direction.

Bottom: Top view.

Tables

Table 1: Summary of the search through the high symmetry sites assuming an undistorted benzene ring. r is the benzene ring radius, d the perpendicular height of the benzene ring above the platinum surface and R the Pendry R -factor. The sites labelled $C_{3v}(\sigma_d)(hcp)$, C_6 and C'_6 produce no r -factor minimum in the tested ranges.

Site	Range r	Range d	Best r	Best d	Minimum R
$C_{2v}(X \rightarrow Y)$	1.33-1.43	2.00-2.55	1.40	2.11	0.1734
$C_{2v}(X \rightarrow X)$	1.30-1.60	2.00-2.55	1.37	2.29	0.3010
$C_{3v}(\sigma_v)(fcc)$	1.38-1.43	2.00-2.55	1.40	2.28	0.2849
$C_{3v}(\sigma_d)(fcc)$	1.33-1.45	2.00-2.55	1.38	2.29	0.5576
$C_{3v}(\sigma_v)(hcp)$	1.33-1.43	2.00-2.55	1.38	2.26	0.3700
$C_{3v}(\sigma_d)(hcp)$	1.38-1.48	2.00-2.55	—	—	—
C_6	1.33-1.43	2.00-2.55	—	—	—
C'_6	1.33-1.43	2.00-2.55	—	—	—

Table 2: The results of the structural search assuming distortions of the benzene ring.

Site	Radii	Angles	d_{Pt-C}	R-Factor
$C_{3v}(\sigma_v)$	$r_1=1.42\text{\AA}$	$\beta=0^\circ$	$2.22\text{\AA}$	0.090
	$r_2=1.42\text{\AA}$	$\theta=-4.5^\circ$		
$C_{2v}(X\rightarrow Y)$	$r_1=1.42\text{\AA}$	$\beta=+2^\circ$	$2.02\text{\AA}$	0.049
	$r_2=1.55\text{\AA}$	$\theta=+6^\circ$		
$C_{2v}(X\rightarrow X)$	$r_1=1.39\text{\AA}$	$\beta=0^\circ$	$2.18\text{\AA}$	0.083
	$r_2=1.39\text{\AA}$	$\theta=-6^\circ$		

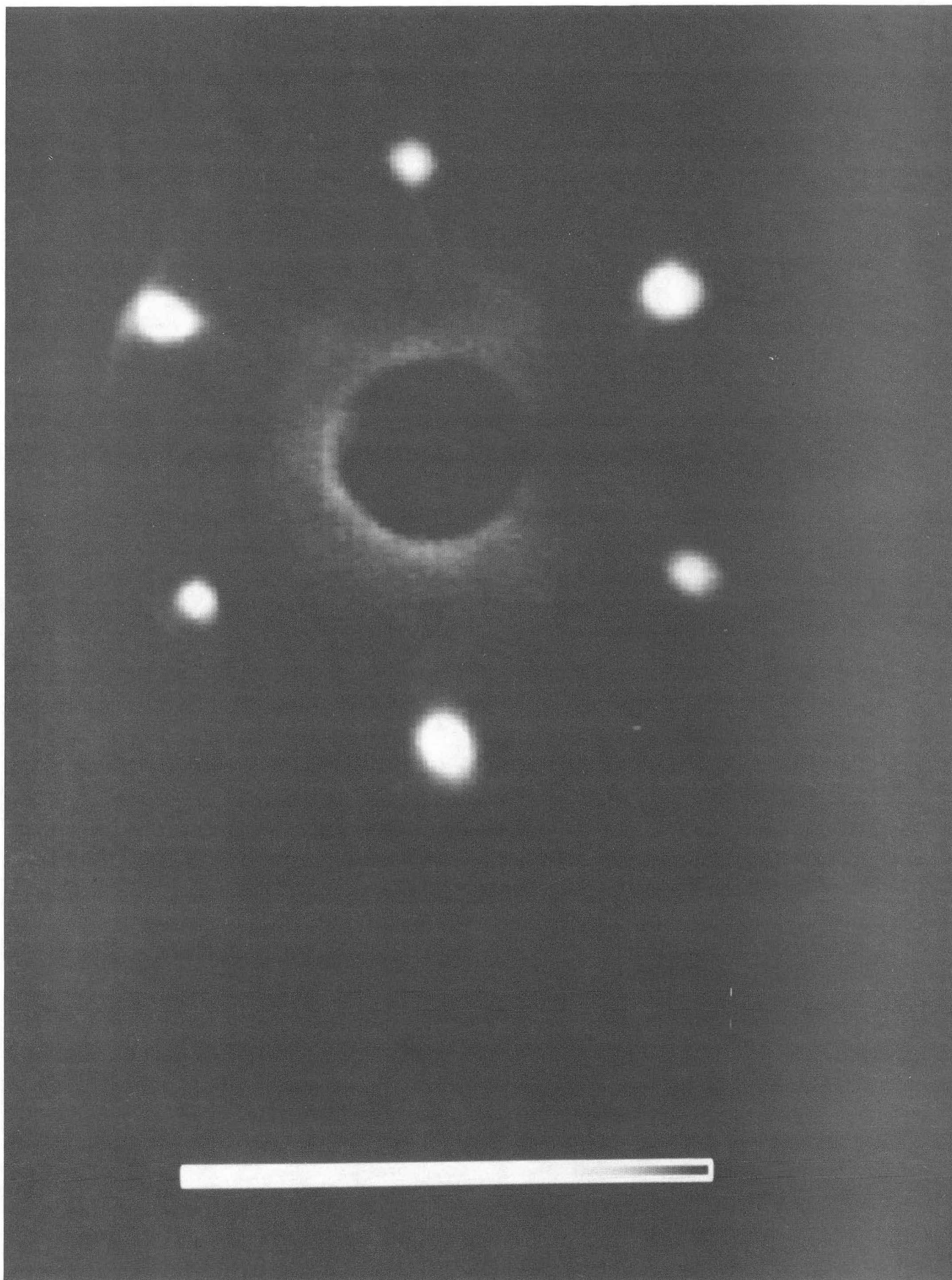


Fig. 1a1

CBB 905-3570

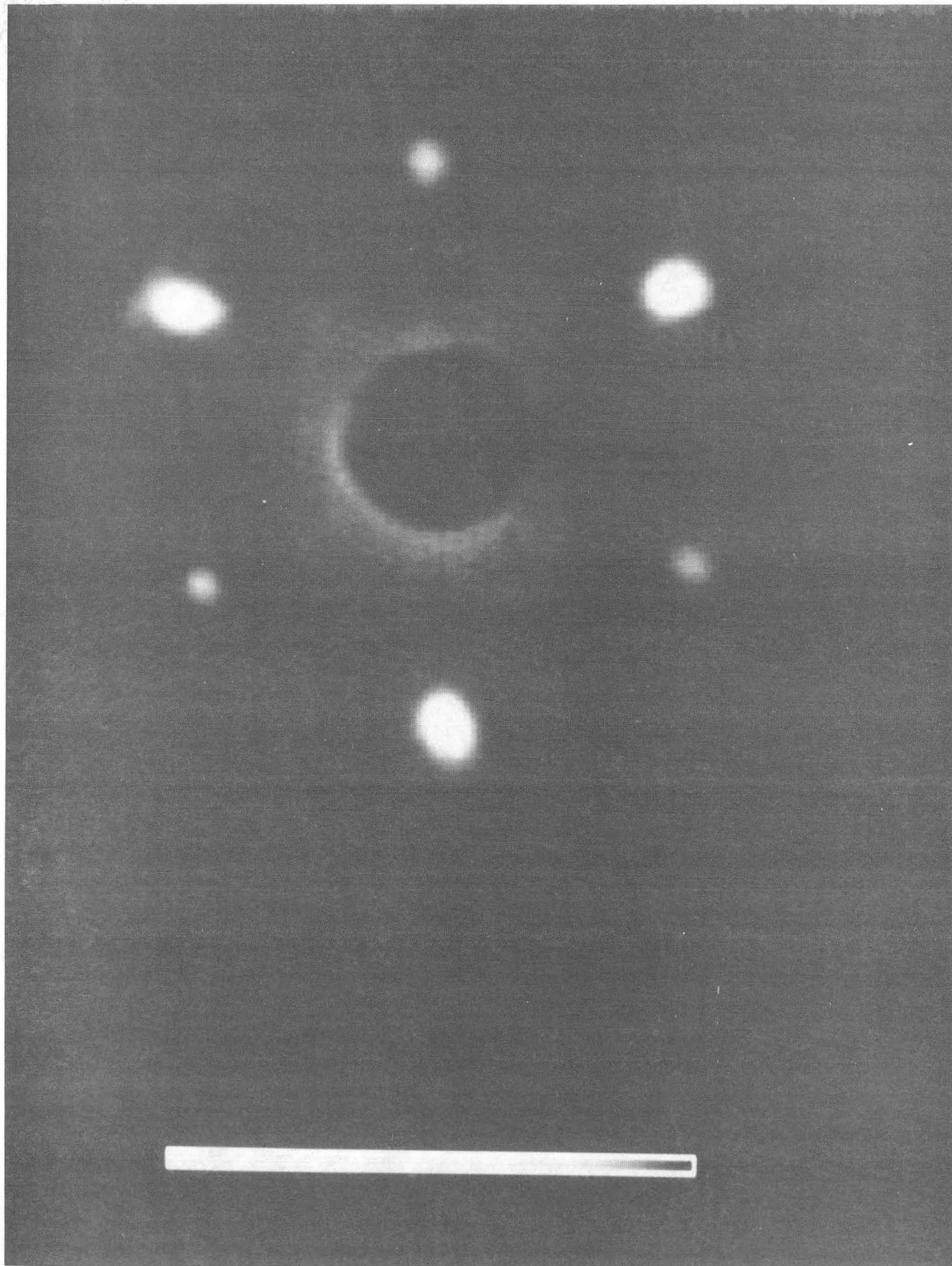


Fig. 1a11

CBB 905-3572

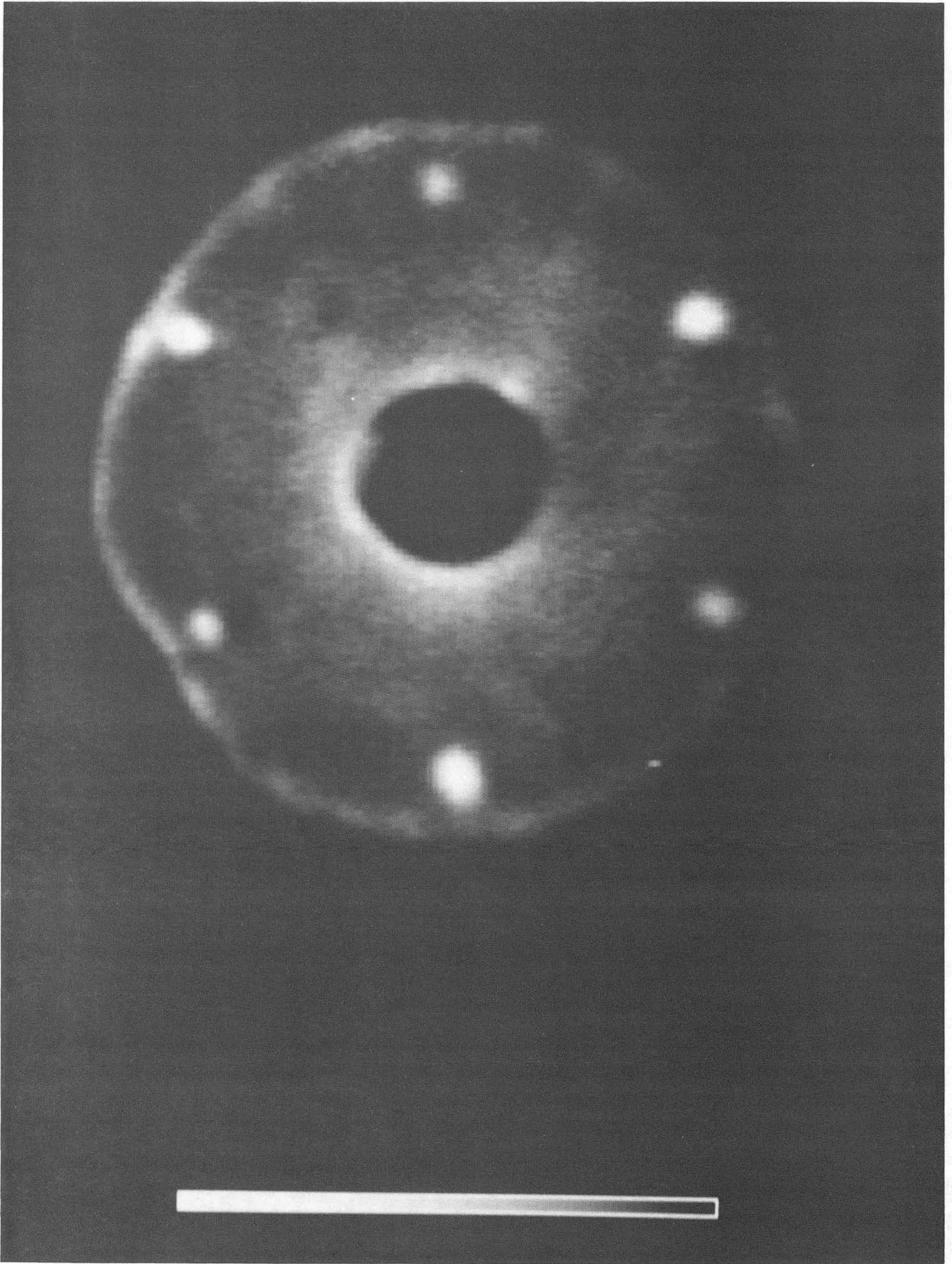


Fig. 1bi

CBB 905-3584

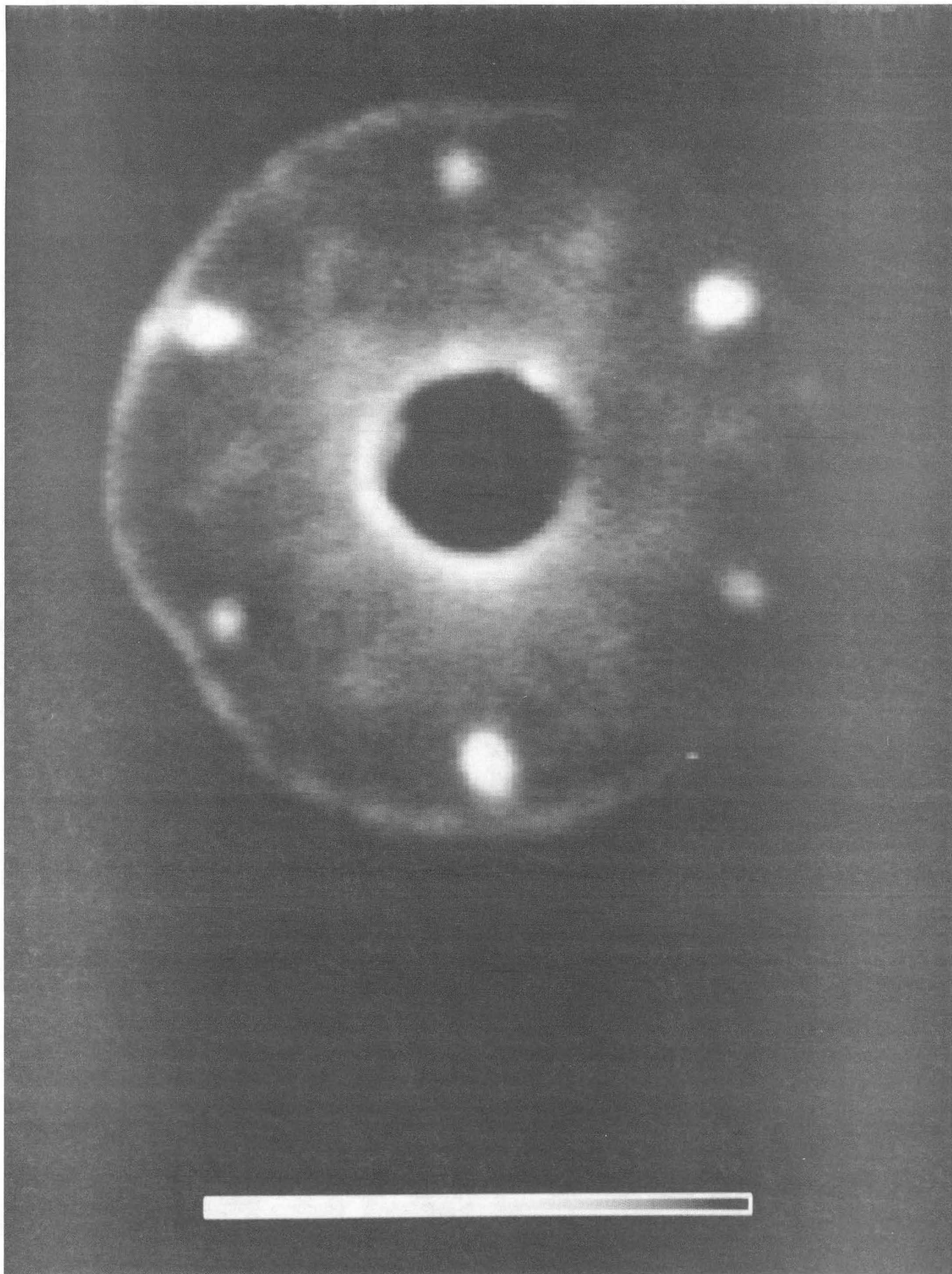


Fig. 1bii

CBB 905-3576

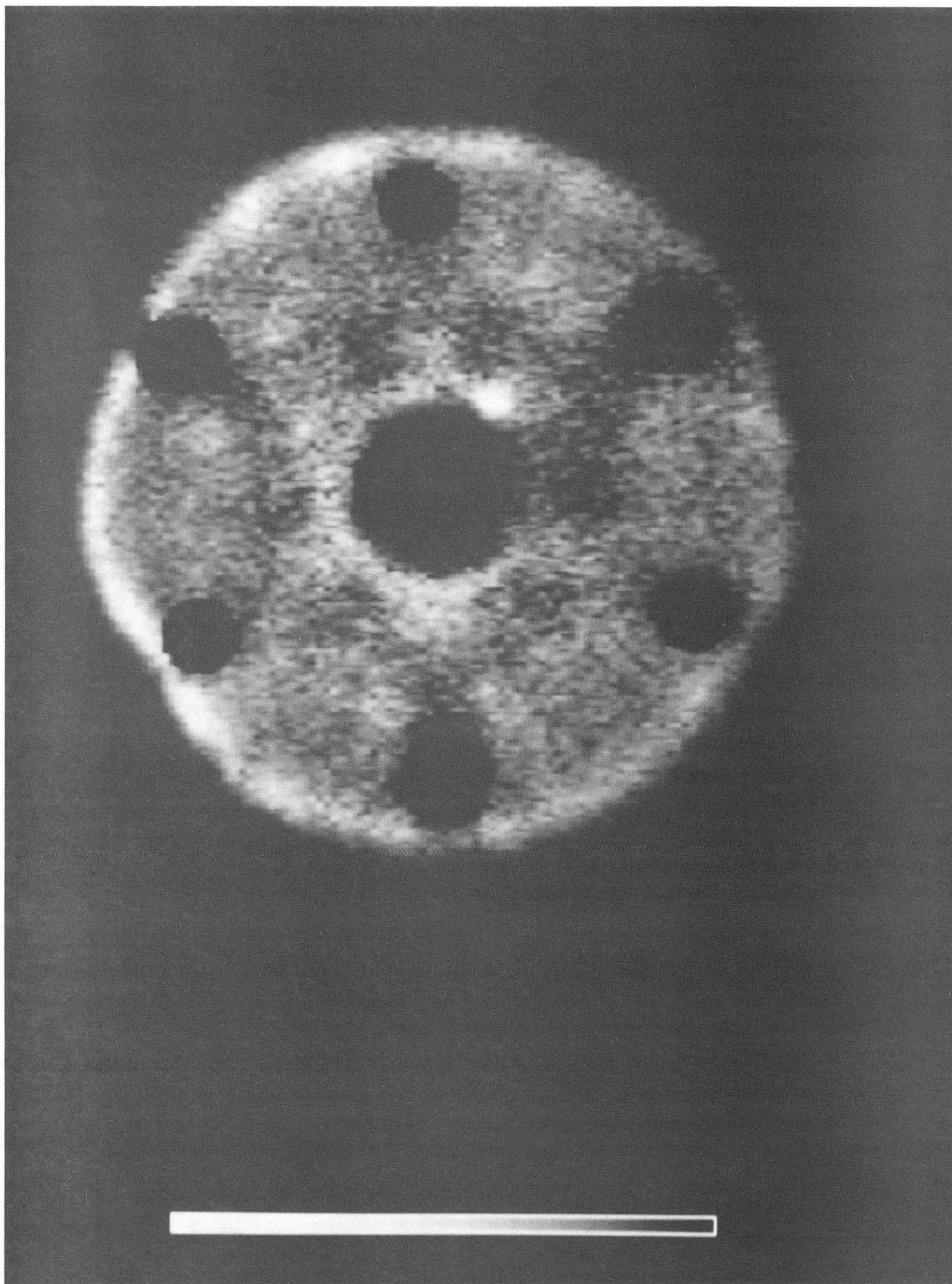
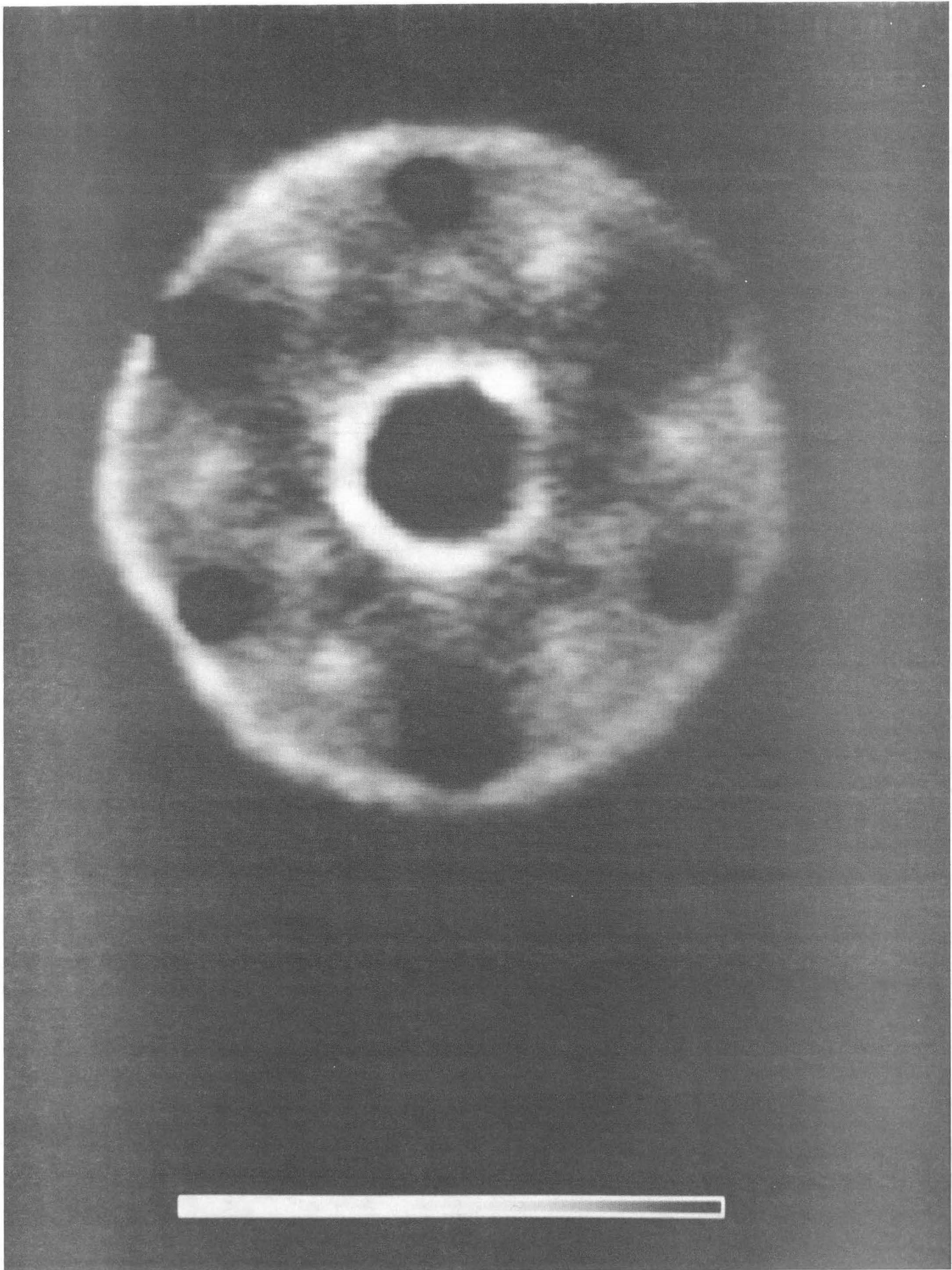


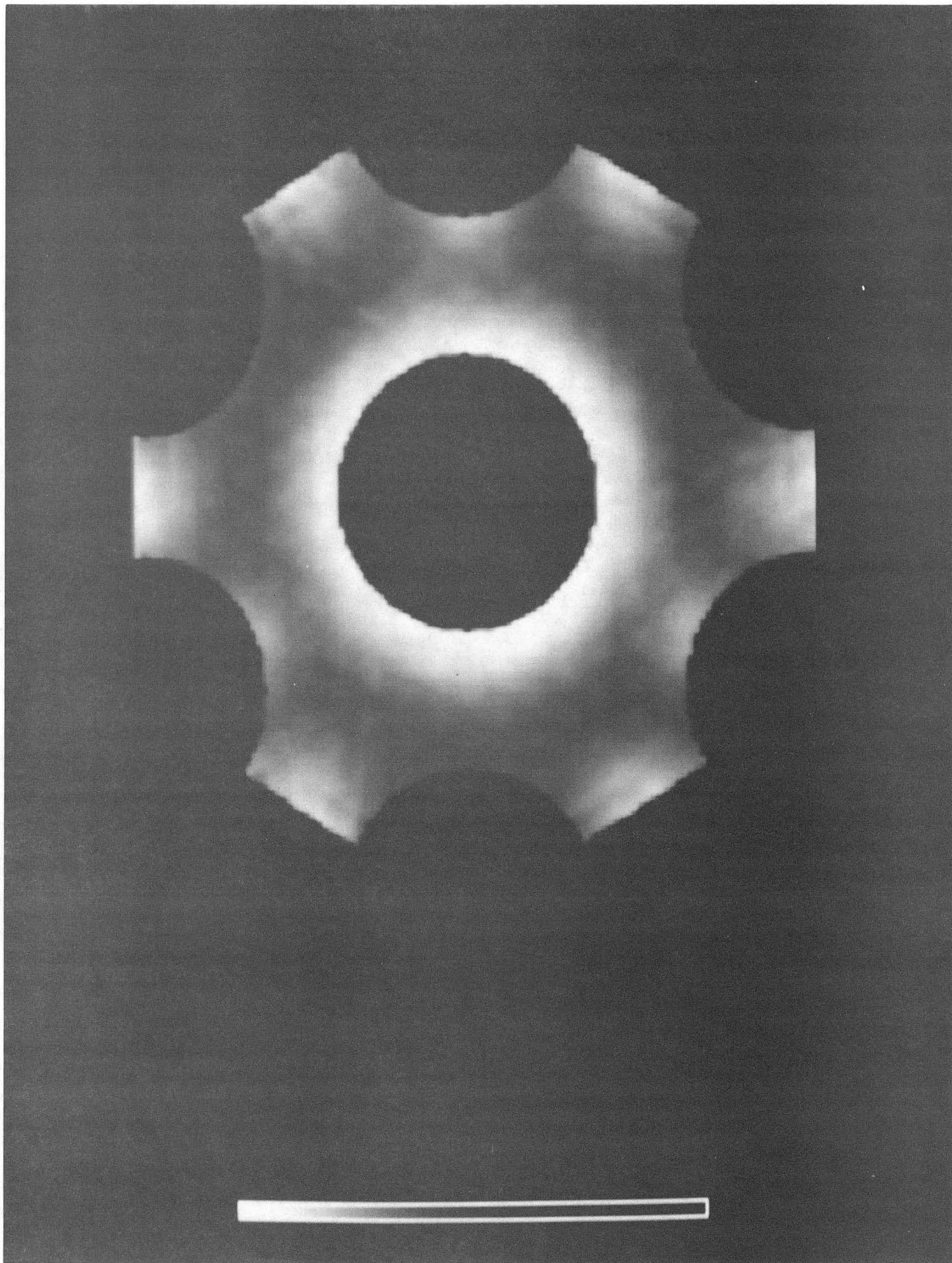
Fig. 2i

CBB 905-3582



CBB 905-3580

Fig. 2ii



XBB 906-5156

Fig. 3a

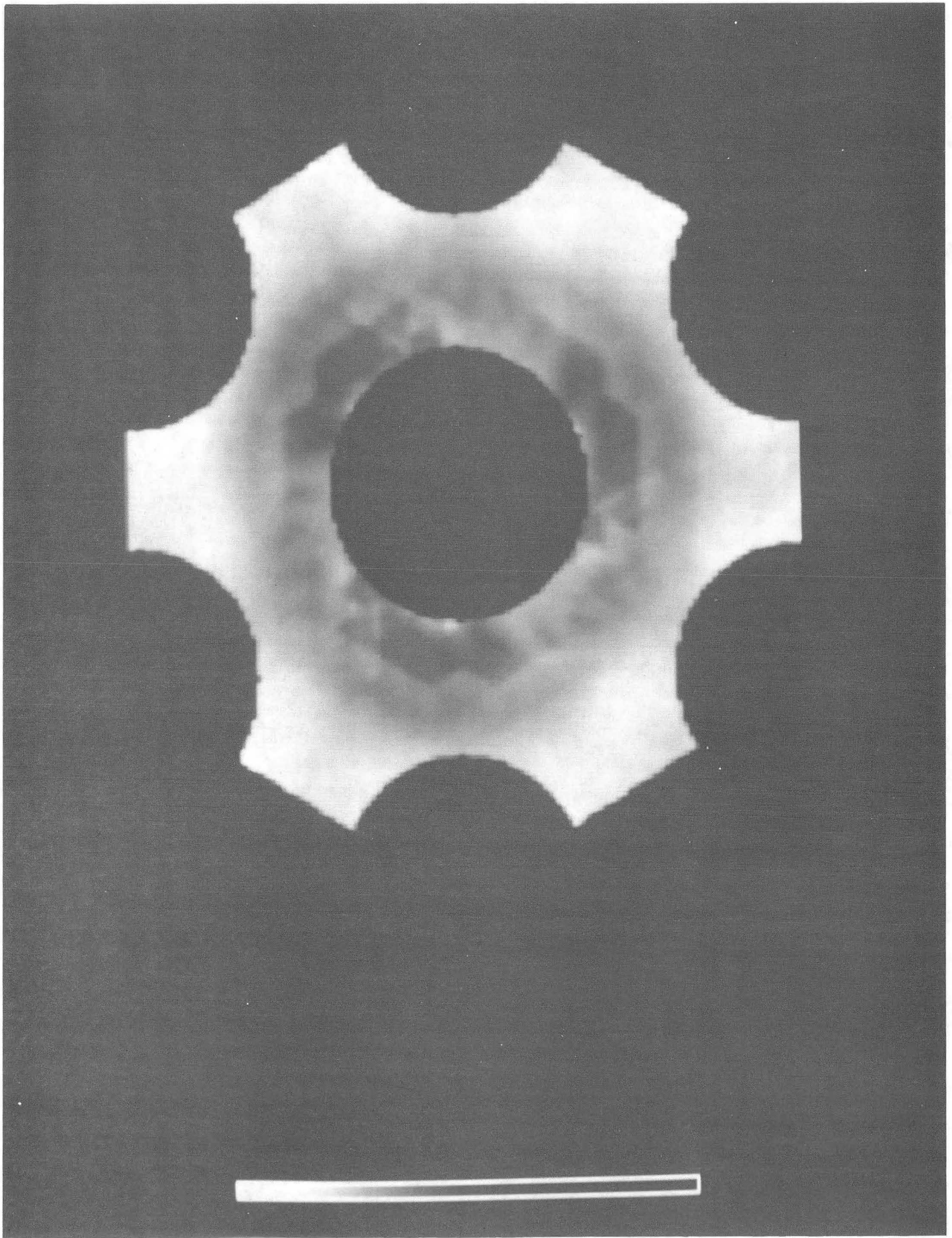
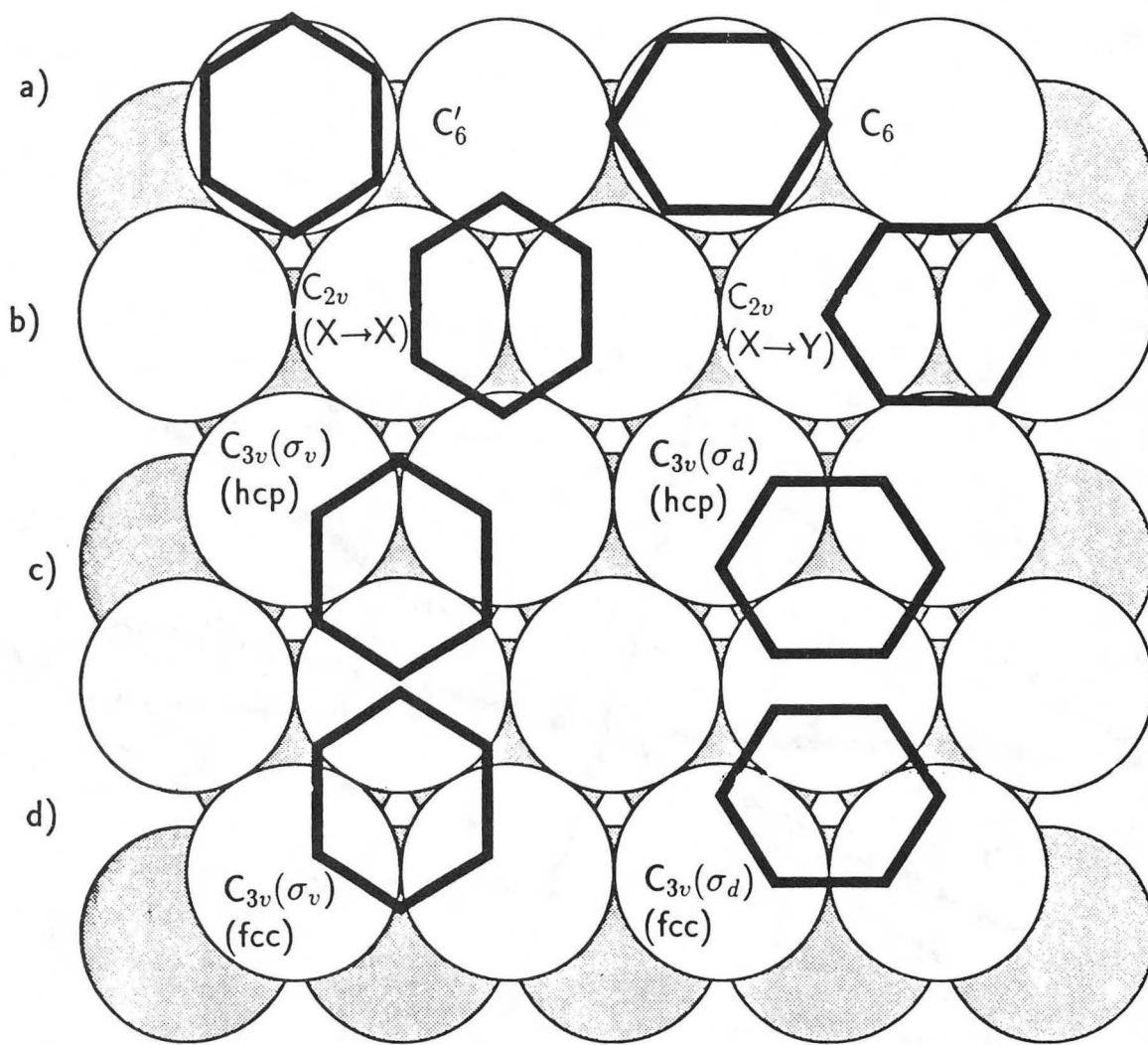


Fig. 3b

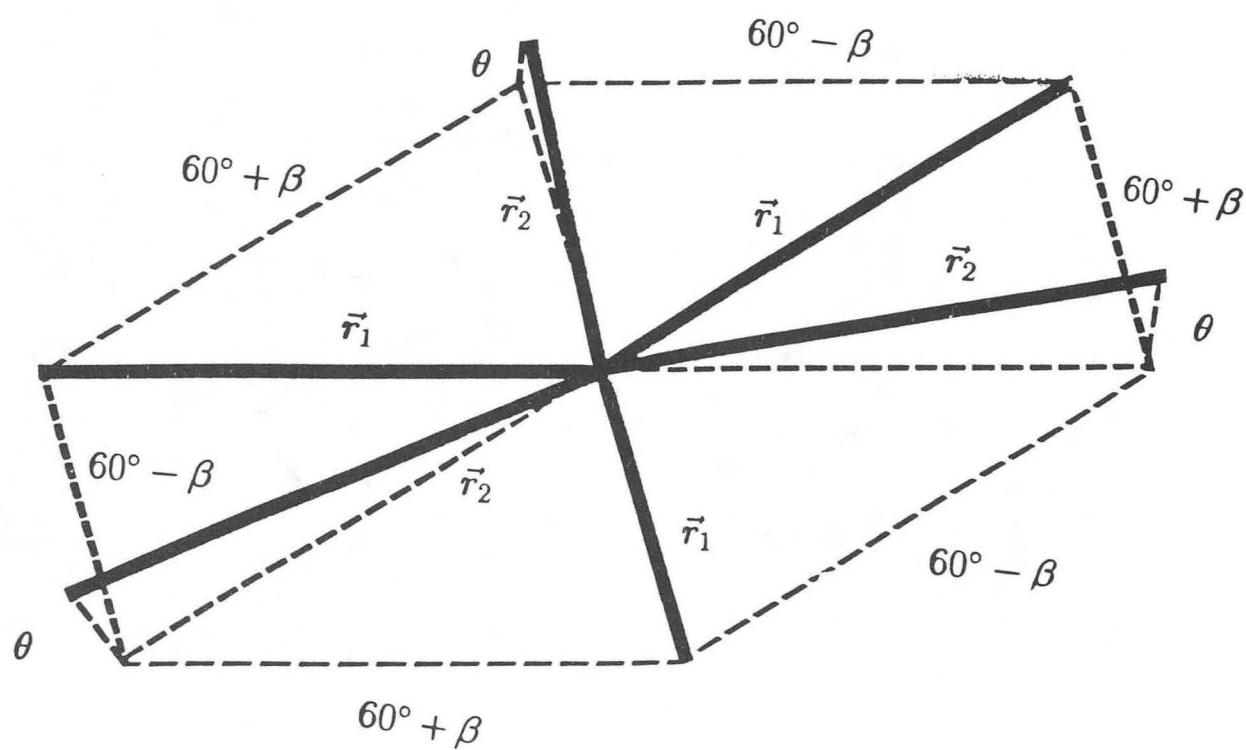
XBB 906-5157



XBL 9011-3574

Fig. 4

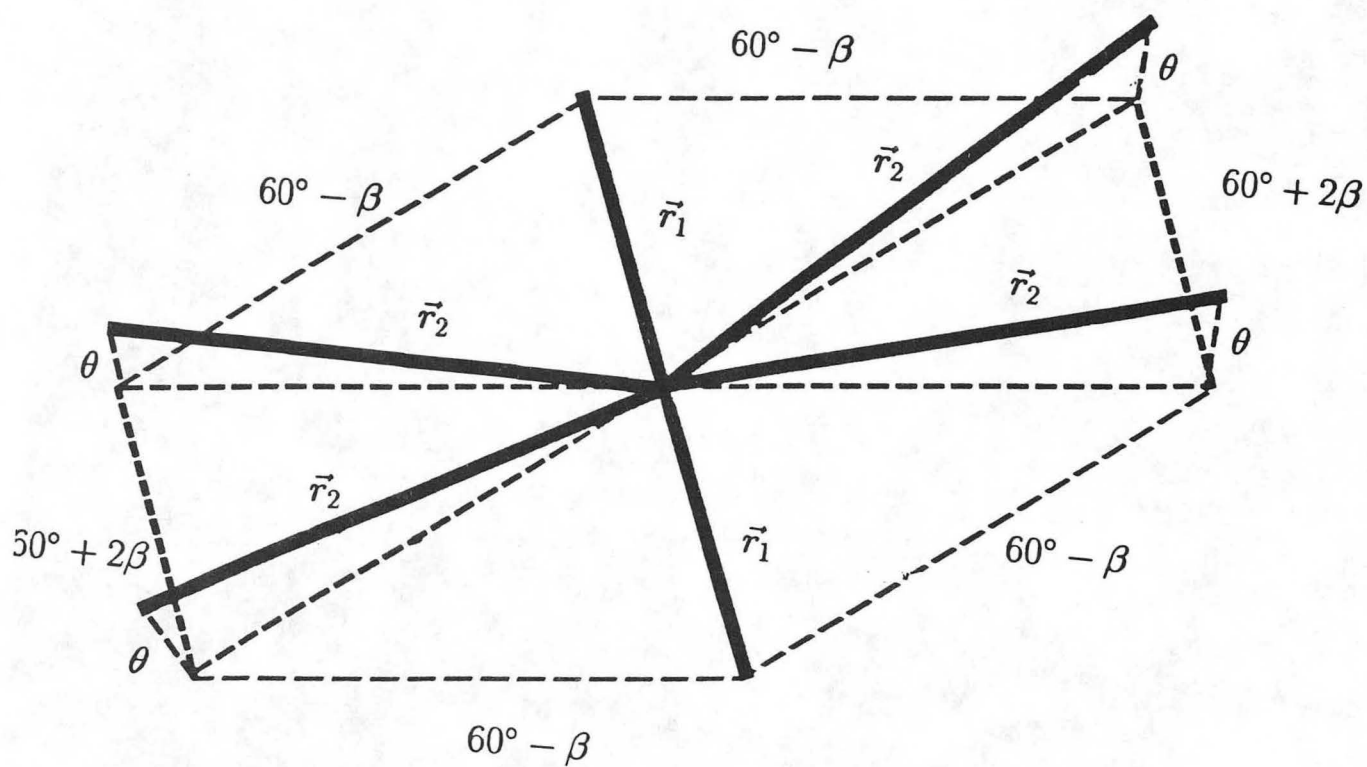
3-fold Symmetry



XBL 9011-3577

Fig. 5a

2-fold Symmetry



XBL 9011-3576

Fig. 5b

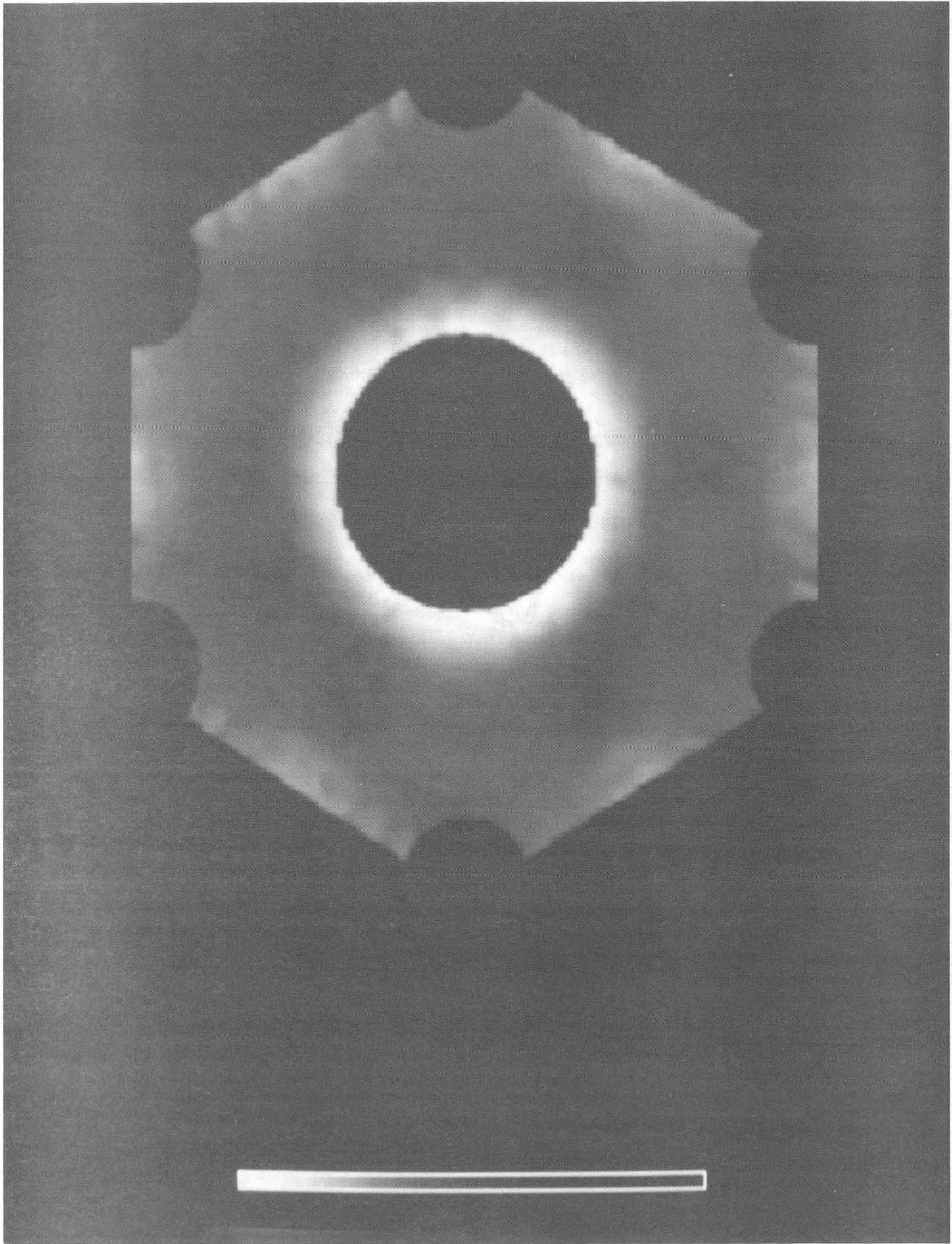
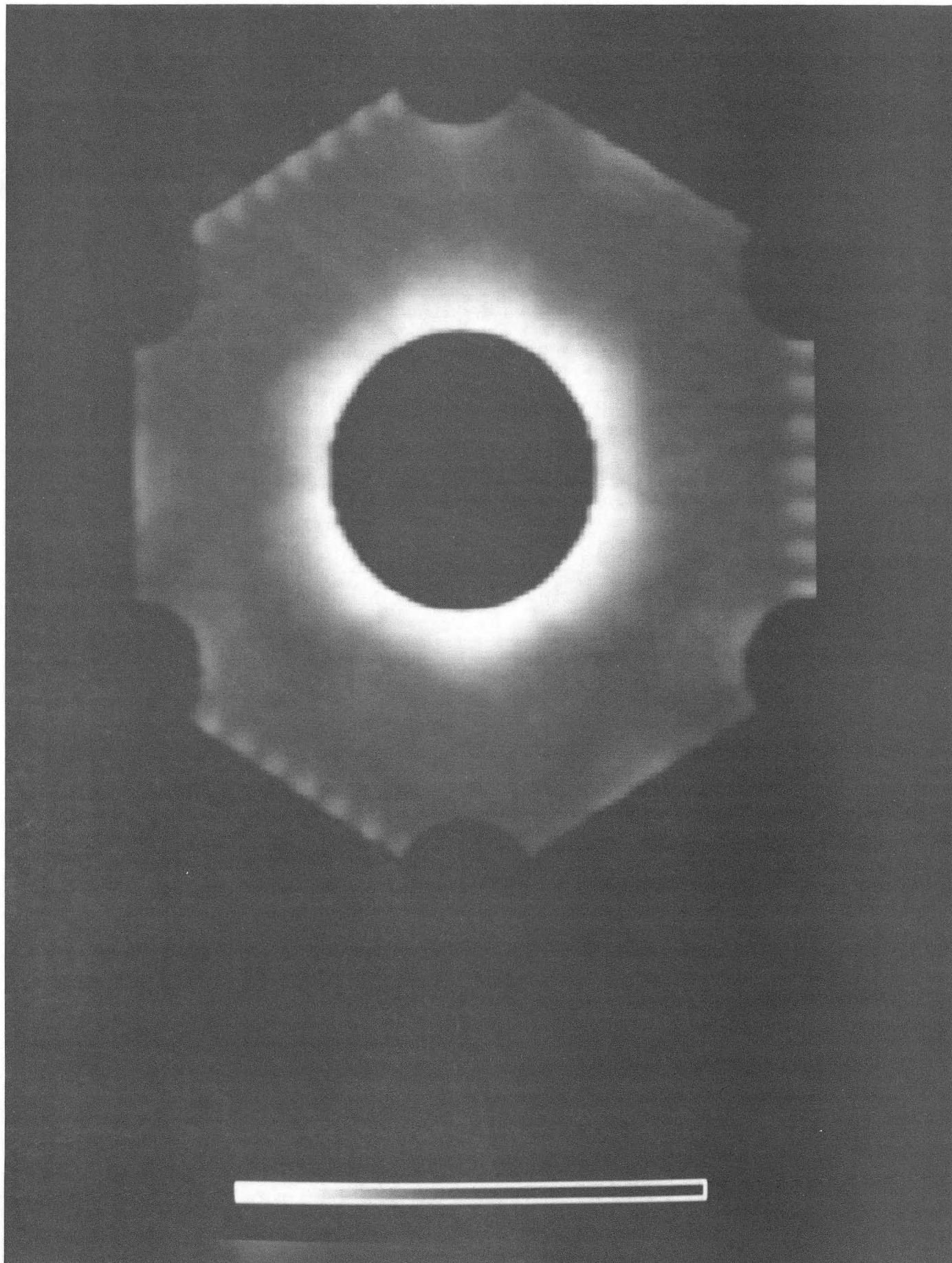


Fig. 6a

XBB 906-5188



XBB 906-5154

Fig. 6b

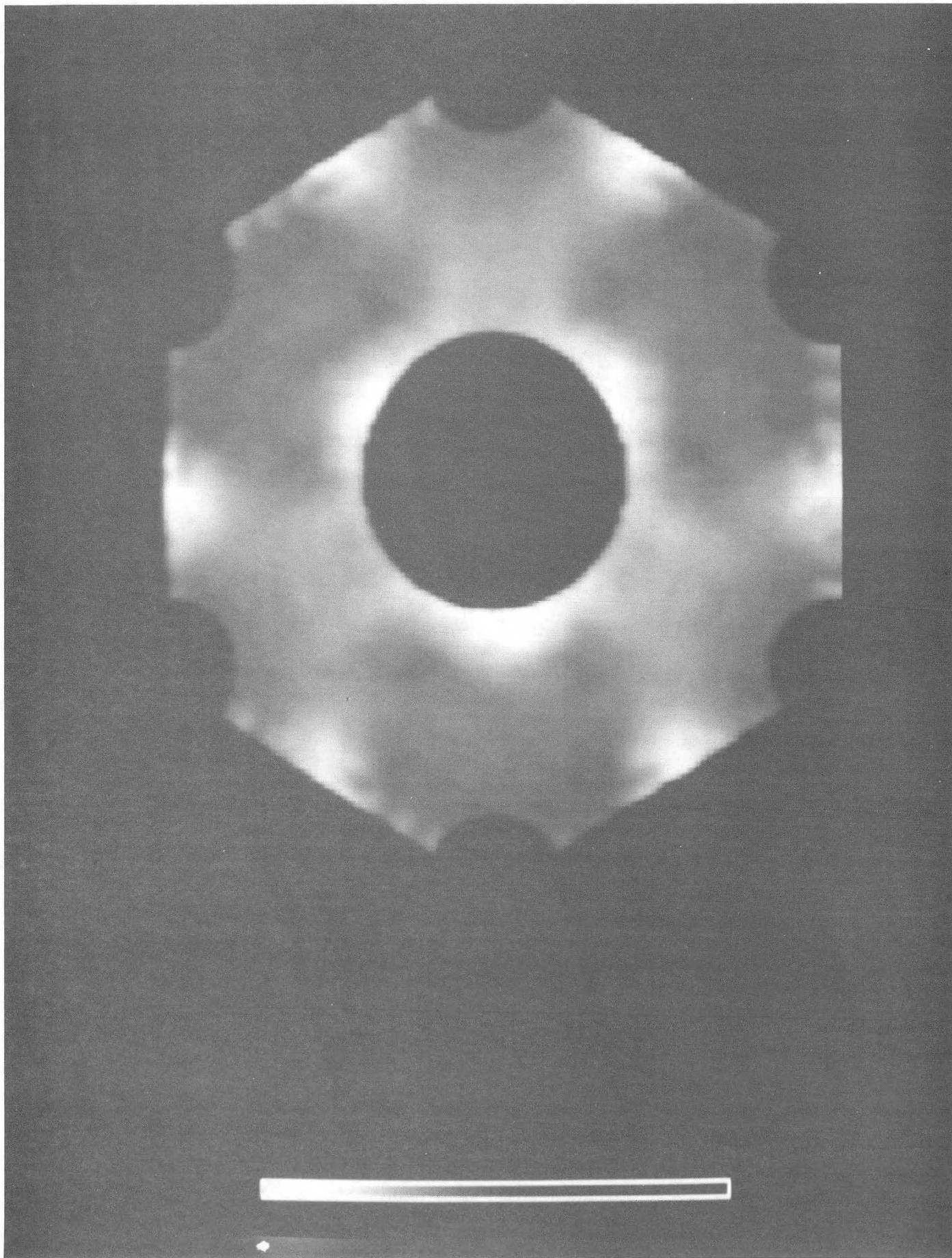
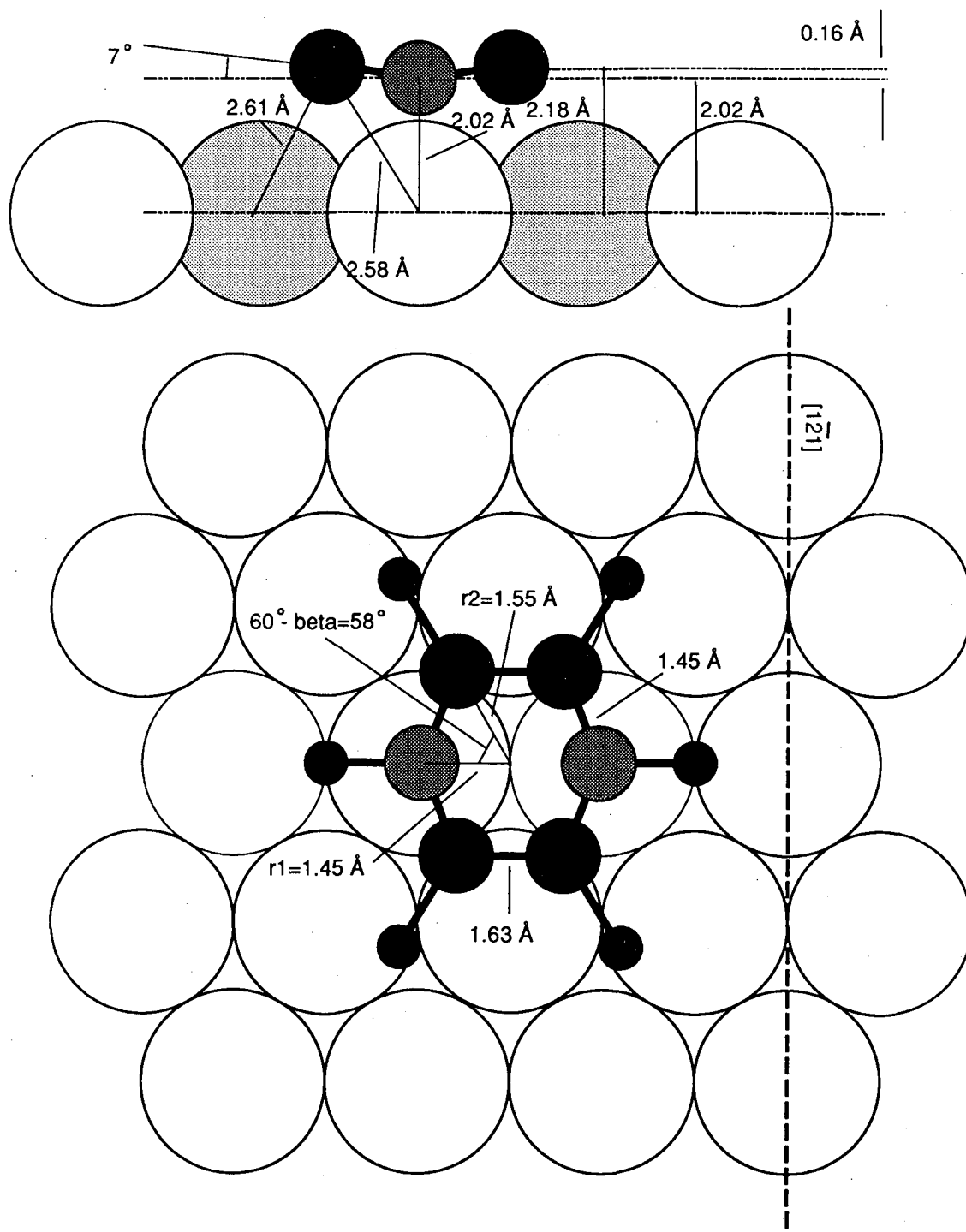


Fig. 6c

XBB 906-5155



XBL 9011-3575

Fig. 7

*LAWRENCE BERKELEY LABORATORY
CENTER FOR ADVANCED MATERIALS
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720*