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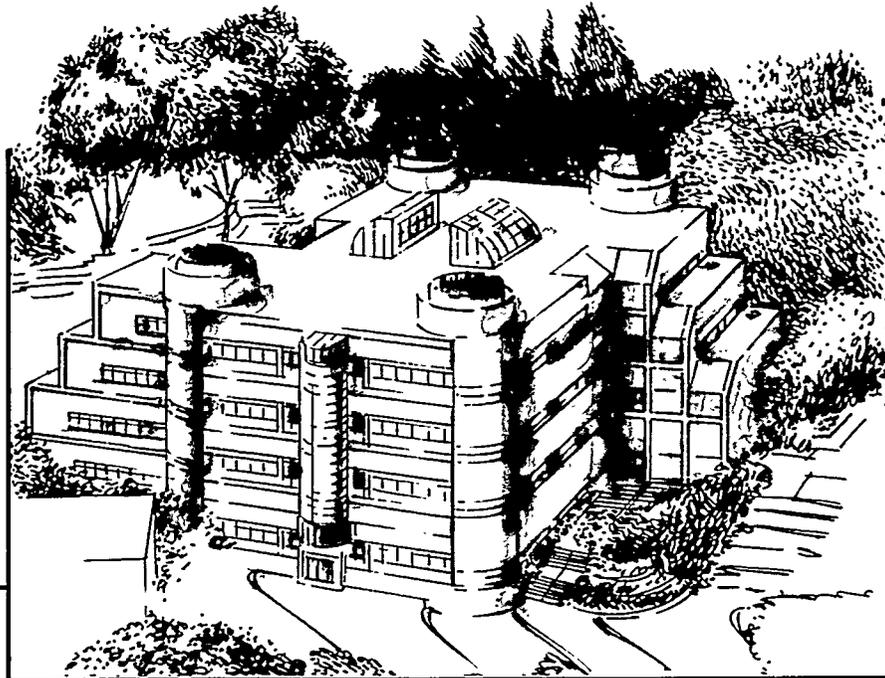
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Scanning Tunneling Microscopy Tip-Dependent Image Contrast of S/Pt(111) by Controlled Atom Transfer

B.J. McIntyre, P. Sautet, J.C. Dunphy, M. Salmeron,
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October 1993



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Scanning Tunneling Microscopy Tip-Dependent Image Contrast of S/Pt(111) by Controlled Atom Transfer

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Sudden changes in the detailed appearance and corrugation of atomic-resolution scanning tunneling microscopy (STM) images are commonly observed. In particular, these effects for the Pt(111)($\sqrt{3} \times \sqrt{3}$)R30°-sulfur structure have been studied. Corrugation changes have been investigated by the controlled transfer of atoms between tip and sample. Theoretical images simulations using electron scattering quantum chemical methods show that the image contrast is strongly dependent on the chemical identity of the STM tip atom. Observed changes in the sulfur images can be explained by changes from platinum-terminated to sulfur-terminated STM tips.

The detailed appearance and corrugation of atomic-resolution scanning tunneling microscopy (STM) images are commonly observed to change suddenly and these changes are usually attributed to random changes in tip structure (gain or loss of atoms). We have studied these effects for the Pt(111)($\sqrt{3} \times \sqrt{3}$)R30°-sulfur structure in a more controlled manner. We have observed dramatic changes in corrugation upon controlled transfer of atoms between the tip and surface (as a result of pulsing the bias voltage). Such transfer of atoms between the tip and surface and bias pulsing has been reported previously.¹ After preparation of the Pt(111)($\sqrt{3} \times \sqrt{3}$)R30°-sulfur structure, the surface was imaged at room temperature in ultrahigh vacuum (UHV). All of the images presented here were obtained with an average current set point of 1.1 nA and a 0.076 V bias. A current mode STM image of the Pt(111)($\sqrt{3} \times \sqrt{3}$)R30°-sulfur structure is shown in Fig. 1(a). In this image, maxima corresponding to sulfur atoms separated by $\sqrt{3} \times$ the Pt-Pt distance are observed. A line profile from point *a* to point *b* shows the current

corrugation is ~ 1 nA [Fig. 1(c)]. After obtaining this image, a 0.7 V bias pulse was applied to three different areas of the image. The previous area was then imaged again [Fig. 1(b)]. In this image, the sulfur areas are much more clearly resolved, and the regions where the tip was pulsed show 6 to 10 missing sulfur atoms each. A line cross section of Fig. 1(b) from point a' to point b' shows the corrugation to be greater than 1 nA [Fig. 1(d)].

To further understand the nature of the tip changes and to confirm the proposed transfer of S atoms from the surface to the tip, we undertook a calculation of the current profiles of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -sulfur structure using the electron scattering quantum chemical (ESQC) method.^{2,3} In this approach, the tunneling gap is treated as a defect in a periodic bulk (tip and sample) across which electrons may propagate or be scattered back. The geometrical structure of the tip and surface is described atom by atom. The model system is comprised of two semi-infinite solids which are generated by repetition of a slab in the z direction. One surface layer, the adsorbates and the tip consisting of a cluster are then inserted between them. This single atom-termination tip cluster was modeled by a tetrahedron of Pt atoms with the apex pointing toward the surface. The system has a finite lateral extension with lateral boundary conditions. The sample, adsorbate, and tip are described by a linear combination of atomic orbitals. The description of the atoms in the bulk has been limited to the $6s$ orbitals for simplicity, while a full spd basis set is used in the surface-adsorbate-tip part where the scattering phenomenon takes place. The energy dependent scattering matrix depends on the detailed structure of the tip, the (x,y,z) coordinates of the tip relative to the surface, and the structure of the surface including atomic and molecular adsorbates. The semiempirical extended Hückel theory is used for the calculation of the Hamiltonian matrix elements on the chosen basis set, while all the overlap matrix elements are exactly calculated. It should be noted that none of

the electronic parameters of the theory has been fitted to experimental STM images. The atomic exponents are obtained from Hartree Fock calculations on the atom while standard atomic energies are used. The gap resistance is derived from the scattering matrix with the Landauer formula using a zero bias voltage approximation. Previous studies using this theoretical approach have shown that the image structure is strongly dependent on the chemical identity of the terminating STM tip atom.^{4,5}

The corrugations obtained after applying the theory to our case are shown by the dashed lines in Figs. 1(c) and 1(d) for tips terminated in Pt and S, respectively. The observed changes in the corrugation of sulfur in our images can thus be explained by changes from platinum-terminated to sulfur-terminated STM tips as shown by the good agreement with theoretically simulated STM corrugations. These results and the holes in image Fig. 1(b) suggest that sulfur is indeed being transferred from the surface to the tip upon bias pulsing and we are observing the resulting changes in corrugation. The origin of the differences in corrugation between S and Pt tips can be qualitatively understood by considering the overlap between tip atom orbitals and the orbitals of the S atoms in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. The 6s external orbitals of Pt atoms extend farther out in space than the smaller S atom 3s and 3p orbitals. As it would be in the case of the experiment, the tip with the Pt atom termination is retracted by $\sim 1.5 \text{ \AA}$ relative to a tip with a sulfur atom termination to maintain the same average tunneling currents. As a result of the more extended overlap, the topographic profiles, or the changes of current in constant height images show much smaller corrugation for the platinum-terminated tip. We have found that we are able to distinguish between two classes of single-atom tips: electronically large metal (Pt, Rh, W, or Re) atoms and smaller main group S or C atoms. We generally observe only small quantitative differences within each class. This method has already been

used in the case of S on Re(0001) recently.⁵ The novelty of the present experiments is the intentional removal of S atoms from the surface by pulsing and their transfer to the tip. A more detailed explanation and discussion of our experimental and theoretical observations of this tip-dependent phenomena is forthcoming.

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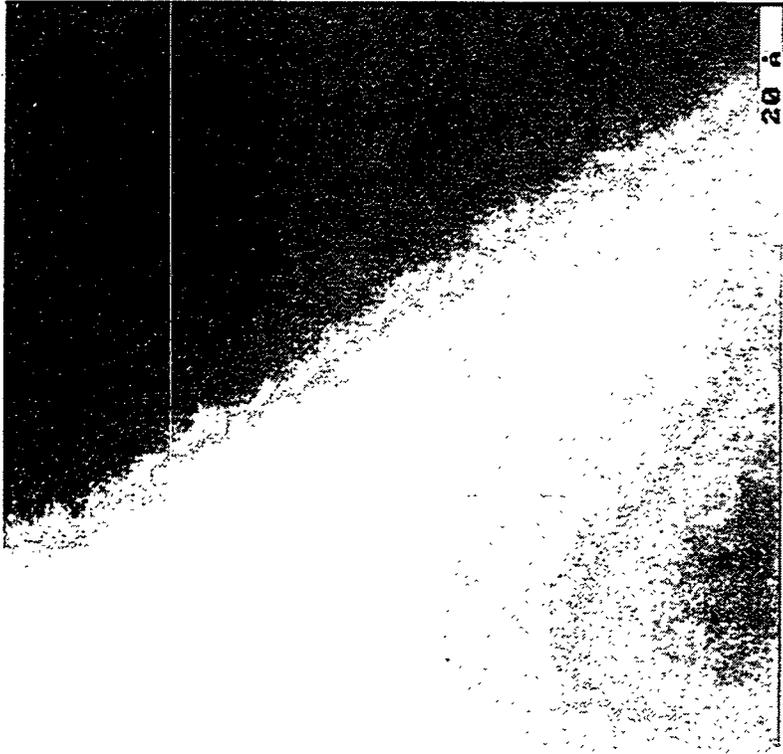
REFERENCES

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- ¹D.M. Eigler, C.P. Lutz, and W.E. Rudge, *Nature* **352**, 600 (1991), and references therein.
- ²P. Sautet and C. Joachim, *Phys. Rev. B* **38**, 12238 (1988).
- ³P. Sautet and C. Joachim, *Chem. Phys. Lett.* **185**, 23 (1991).
- ⁴P. Sautet and C. Joachim, *Ultramicroscopy* **42**, 115 (1992).
- ⁵J.C. Dunphy, D.F. Ogletree, M.B. Salmeron, P. Sautet, M.-L. Bocquet, and C. Joachim, *Ultramicroscopy* **42-44**, 490 (1992).

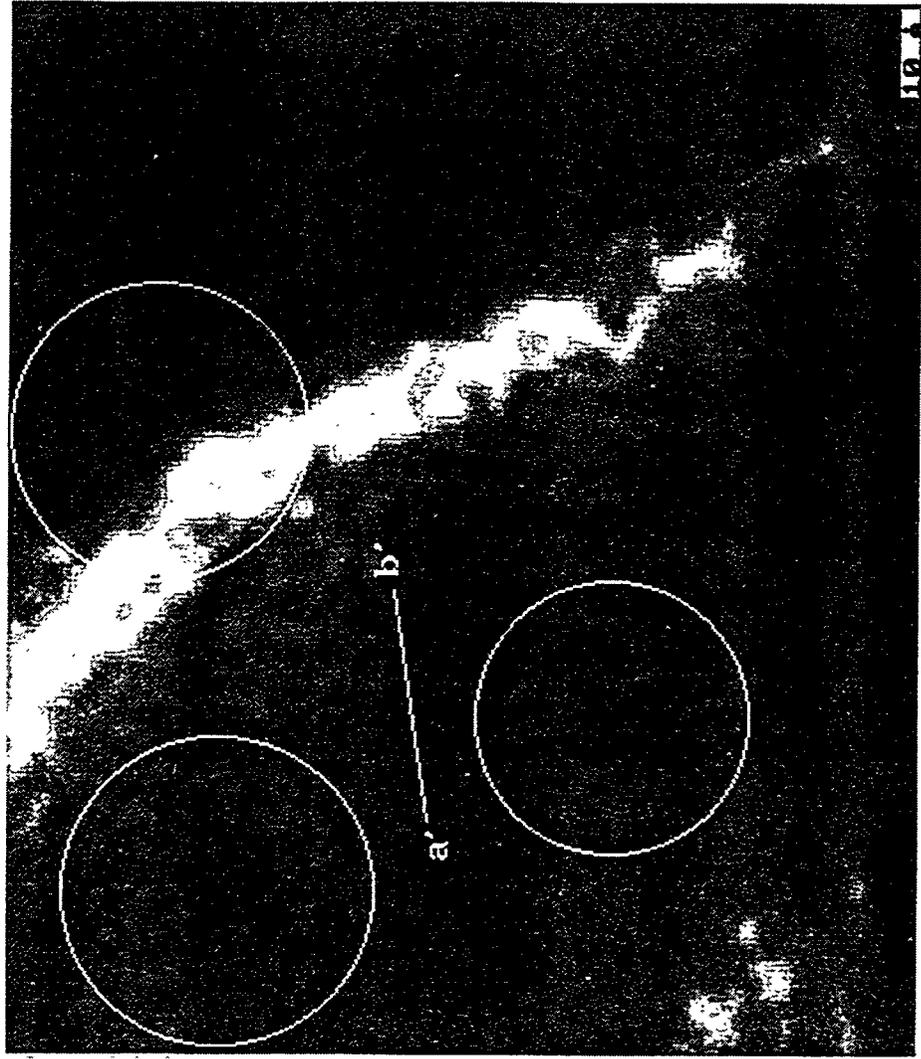
FIGURE CAPTIONS

FIG. 1. (A) Current mode STM image of Pt(111)($\sqrt{3} \times \sqrt{3}$)R30°-S. In this image, the sulfur atoms are resolved, however, the corrugation is weak (approx. 0.1 nA) as shown in the line cross section from point *a* to point *b* [(C)]. A step runs from the top center to the bottom right of the image. (B) Current mode STM image of the same area as (A) after applying a 0.7 V bias pulse in each of three different areas that removed 6 to 10 S atoms (circled). In this image, the sulfur atoms are clearly resolved and the three locations where the bias was pulsed show missing sulfur. (C) Line cross section of (A) from point *a* to point *b*, showing the corrugation to be ~0.1 nA. The dotted line shows the calculated corrugation profile for tips terminated in a single Pt atom. The ESQC method described in Refs. 2-4 was used for the calculation. (D) Line cross section of (B) from point *a'* to point *b'*, showing the corrugation to be greater than 1 nA. The dotted line shows the calculated corrugation profile for tips terminated in a single S atom.

A



B



Figs. 1(a) and 1(b)

C

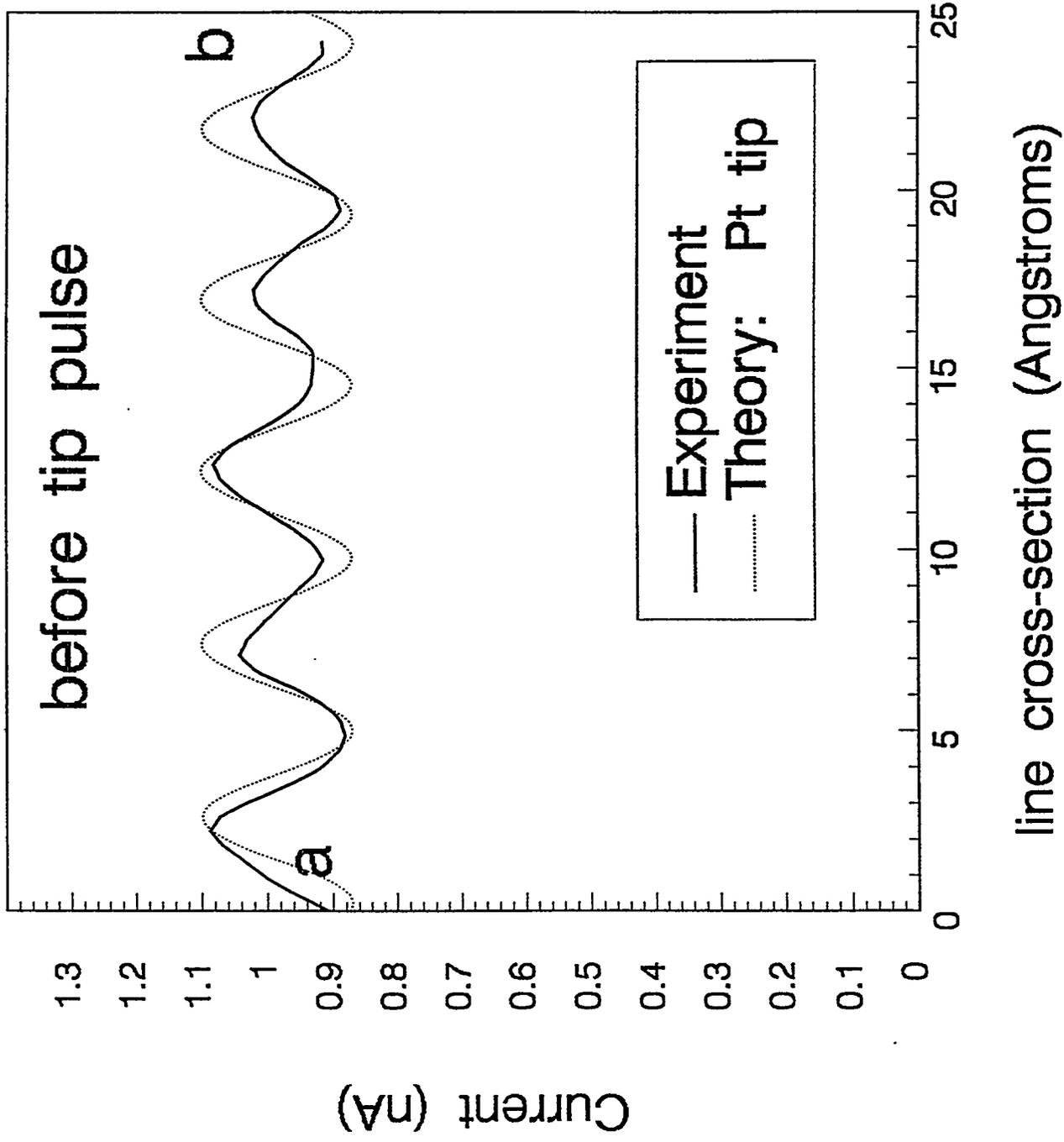


Fig. 1(c)

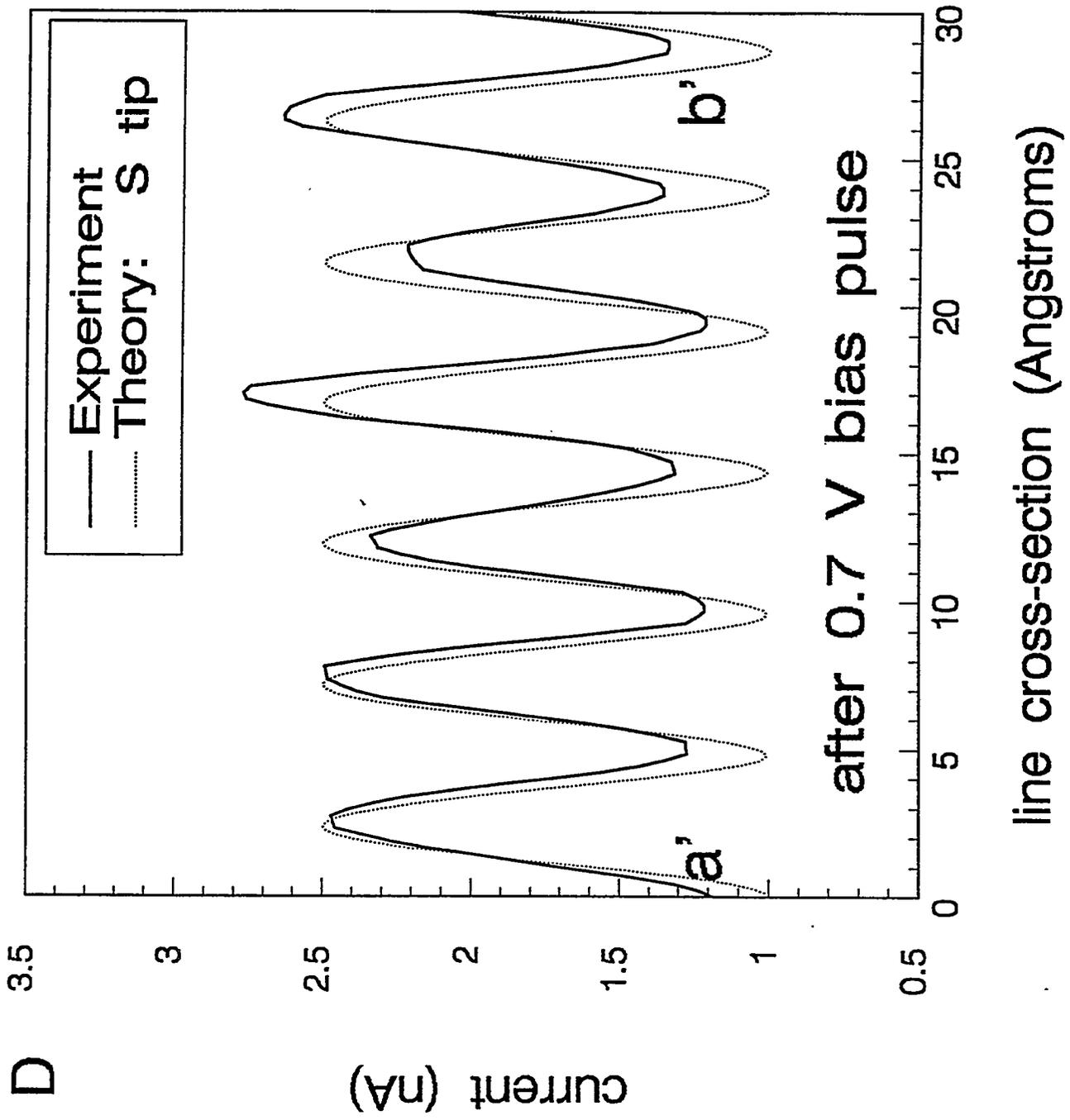


Fig. 1(d)