Comment on "Adsorbate Structures from Photoelectron Diffraction: Holographic Reconstruction or Real-Space Triangulation?"

In a recent Letter, Dippel *et al.* [1] have proposed a method for adsorbate structure elucidation based on the behavior of backscattered photoelectrons at low kinetic energies ($\simeq$50–400 eV). They note that peaks (valleys) in a scanned-energy photoelectron diffraction curve for a two-atom system such as emitter E and scatterer S_1 in Fig. 1(a) from which photoelectrons are observed near the backscattering condition (i.e., for θ near 90°) represent constructive (destructive) interference conditions, and thus that a θ scan in the constructive (destructive) condition yields a peak (valley) directly along the bond direction. They proposed to extend this idea to the nearest-neighbor backscatterers of a real adsorbate on a multi-atom substrate. The authors recognized possible complications that could arise due to the presence of other large-angle near-neighbor backscatterers away from the two-atom backscattering direction, and suggested correcting for such effects by using θ-dependent constructive/destructive intensity ratios collected at energies appropriate to the two-atom system.

In this Comment, we point out that diffraction effects due to such large-angle near-neighbor scatterers could, for an important class of realistic bonding geometries, be strong enough to make this method invalid. To explore this, we first performed scanned-energy photoelectron diffraction simulations over the interval 90–400 eV for a Ni scatterer placed 2.0 Å directly behind an $s \rightarrow p$ emitter [the two-atom cluster of E and S_1 in Fig. 1(a)] [2]. Analogous simulations were then performed on a cluster including four additional near-neighbor scatterers S_2 in a square pattern. The E to S_2 distance d was varied systematically from 1.8 Å to 2.8 Å in 0.1 Å steps by moving the S_2 scatterers radially outwards. Following Dippel *et al.*, we then averaged six constructive/destructive intensity ratios (A/B', B/C', B/B', C/C', A/C', and C/B' of Fig. 1 in Ref. [1]), and these averages are shown as a function of θ for various d values in the solid curves of Fig. 1(b).

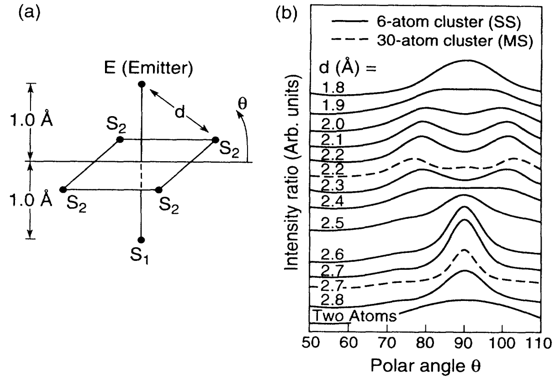

FIG. 1. (a) Six-atom cluster used in simulations. (b) Average of six constructive/destructive intensity ratios as a function of θ and d. Solid curves calculated for the six-atom cluster in single scattering; dashed curves for a larger thirty-atom cluster with more extended substrate and in multiple scattering. The analogous average ratio for the two-atom $E+S$ cluster is shown as the bottom curve.

If the method of Dippel *et al.* is to be universally reliable, a peak should always be found for $\theta = 90°$ in these constructive/destructive intensity ratios. However, for the reasonable bond length range of 2.0–2.3 Å for which destructive interference occurs between waves scattered from the four scatterers S_2 and that from the backscatterer S_1, this is not the case, and the bond direction would be misestimated by as much as ±13°. Also shown in Fig. 1(b) are dashed curves for a much larger cluster of thirty atoms which should include all important scatterers [3], as calculated in multiple scattering; the same general behavior is seen. Finally, we note that geometries very close to that of Fig. 1(b) with next-nearest-neighbor to nearest-neighbor distances in the ratio of 1.0–1.1 are indeed found for real atomic adsorbate cases such as C/Ni(001), N/Ni(001), O/Cu(001), and O/Cu(110) (see e.g., Refs. [13], [15], and [16] in [1]).

We thus believe that this method should be applied with considerable caution, as it seems certain that anomalous cases will arise for which the real-space triangulation proposed will lead to significant errors. The use of holographic reconstructions that is criticized by comparison in this Letter thus remains in our opinion a fruitful alternative approach for the first step of an adsorbate structure determination.

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[1] R. Dippel, D. P. Woodruff, X.-M. Hu, M. C. Asensio, A. W. Robinson, K.-M. Schindler, K.-U. Weiss, P. Gardner, and A. M. Bradshaw, Phys. Rev. Lett. **68**, 1543 (1992).
[2] Calculations were initially performed at a single scattering level, but we have verified that the inclusion of multiple scattering does not change any of our basic conclusions. The photoelectron emission direction was kept parallel to the light polarization. The methodology used is discussed in A. P. Kaduwela, D. J. Friedman, and C. S. Fadley, J. Electron Spectrosc. Relat. Phenom. **57**, 223 (1991).
[3] M. Sagurton, E. L. Bullock, and C. S. Fadley, Surf. Sci. **182**, 287 (1987), especially Fig. 5.

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